Some New Properties of Chiral Molecules

by

Caroline J. Johnston

B.Sc. (Glasgow)

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Supervisor:
Prof. L. D. Barron.

Dept. of Chemistry,
University of Glasgow.

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Abstract

The work in this thesis divides naturally into two distinct parts which are linked by the general underlying theme of chiral discrimination. The first part concerns the discriminatory response of chiral molecules to circularly polarized light which constitutes optical activity, the second, chiral discrimination in intermolecular forces.

Specifically, in Part I, a detailed study of rotational optical activity is undertaken. Expressions are derived to describe Raman optical activity, optical rotation and circular dichroism by first treating the simple case of a symmetric top molecule and then allowing this to be the basis for the more sophisticated development required for an asymmetric top molecule.

In Part II, discrimination in the dispersion interaction between odd-electron chiral molecules is studied. It is shown that novel contributions to the discriminatory interaction are introduced by allowing for the time-odd part of the molecular optical activity tensor which is supported by chiral molecular systems in which there is some source of time asymmetry, as provided, for example, by the residual electronic angular momenta of odd-electron molecules. Both a semi-classical and a quantum electrodynamical treatment are given, the latter making possible a study of the wave-zone region in which the finite speed of light must be taken into account. Calculations, within the semi-classical model, on a hypothetical odd-electron chiral transition metal complex of O^* symmetry indicate that the new discriminatory contributions could be within an order of magnitude of the conventional discriminatory contributions.

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1.1 Introduction

Optical activity associated with electronic and vibrational transitions has been extensively studied [1-5]. While this has proven a fertile area of theoretical and experimental research, the possibility of optical activity in rotational transitions has been little considered.

For a fluid in the absence of an orientating influence, such as an external magnetic field, the conventional procedure is to average the expression for a particular optical activity parameter over all orientations of the molecule. Since this isotropic average is equivalent to a quantum-statistical average over all rotational states, information about individual rotational transitions is lost. The first treatment of optical activity to take account of contributions from rotational transitions in a non-classical way was that given by Chui of optical rotation in symmetric tops [6]. Later work in rotational optical activity has included further studies of optical rotation [7-9] and a consideration of Raman optical activity (ROA) [10] and circular

dichroism (CD) [11]. While all these effects originate in the discriminatory response of a chiral molecule to right and left circularly polarized light, each is associated with a different physical phenomenon; optical rotation with refraction, CD with absorption and ROA with Raman scattering.

In this chapter we shall present a quantum mechanical development of rotational ROA in symmetric top molecules.

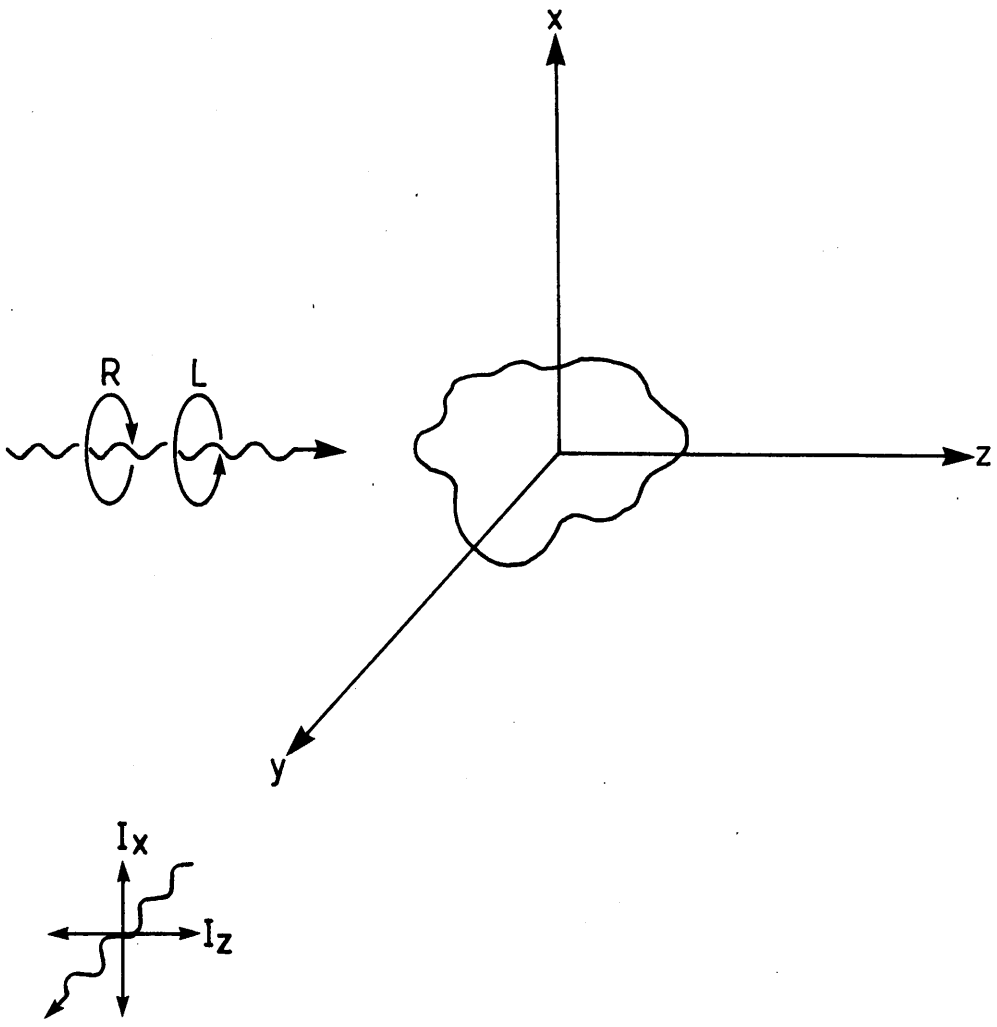
1.2 Theory

1.2.1 Basic definitions and expressions

We shall consider the experimental arrangement of incident light, observed scattered light and sample depicted in fig. 1.1, in which circularly polarized light propagates along the z direction and the scattered radiation is detected at 90^o along the y direction. An appropriate measure of Rayleigh and Raman optical activity is the dimensionless circular intensity difference (CID)

$$\Delta_\alpha = (I_\alpha^R - I_\alpha^L)/(I_\alpha^R + I_\alpha^L) \tag{1.1}$$

where I_α^R and I_α^L are the intensities of scattered light with α polarization in right and left circularly polarized incident light [1]. To obtain the polarized ($\alpha = x$) and depolarized ($\alpha = z$) Rayleigh CIDs in terms of molecular property tensors requires second-order time-dependent perturbation theory to calculate the electric and magnetic multipole moments induced in a molecule by the incident light. These induced moments are then taken to be the source of the scattered radiation. All calculations can be carried out adequately using semi-classical methods; that is, we may treat molecules as quantum mechanical entities interacting with classical electromagnetic fields.



The geometry of polarized light scattering at 90°

Fig. 1.1

The Rayleigh circular intensity sums and differences are found to be [1,12]

$$I_x^R + I_x^L = \frac{\omega^4 \mu_o E^{(0)^2}}{32\pi^2 cy^2}(\tilde{\alpha}_{xx}\tilde{\alpha}^*_{xx} + \tilde{\alpha}_{xy}\tilde{\alpha}^*_{xy} + \cdots) \tag{1.2a}$$

$$I_z^R + I_z^L = \frac{\omega^4 \mu_o E^{(0)^2}}{32\pi^2 cy^2}(\tilde{\alpha}_{zx}\tilde{\alpha}^*_{zx} + \tilde{\alpha}_{zy}\tilde{\alpha}^*_{zy} + \cdots) \tag{1.2b}$$

$$\begin{aligned} I_x^R - I_x^L = \frac{\omega^4 \mu_o E^{(0)^2}}{16\pi^2 c^2 y^2}[&\mathrm{Im}(c\tilde{\alpha}_{xy}\tilde{\alpha}^*_{xx} + \tilde{\alpha}_{xy}\tilde{G}^*_{xy} + \tilde{\alpha}_{xx}\tilde{G}^*_{xx} \\ &-\tilde{\alpha}_{xy}\tilde{\mathcal{G}}^*_{xz} + \tilde{\alpha}_{xx}\tilde{\mathcal{G}}^*_{yz}) + \frac{1}{3}\omega\mathrm{Re}(\tilde{\alpha}_{xx}\tilde{A}^*_{xzy} \\ &-\tilde{\alpha}_{xy}\tilde{A}^*_{xzx} + \tilde{\alpha}_{xy}\tilde{\mathcal{A}}^*_{xxy} - \tilde{\alpha}_{xx}\tilde{\mathcal{A}}^*_{yxy}) + \cdots] \end{aligned} \tag{1.2c}$$

$$\begin{aligned} I_z^R - I_z^L = \frac{\omega^4 \mu_o E^{(0)^2}}{16\pi^2 c^2 y^2}[&\mathrm{Im}(c\tilde{\alpha}_{zy}\tilde{\alpha}^*_{zx} + \tilde{\alpha}_{zy}\tilde{G}^*_{zy} + \tilde{\alpha}_{zx}\tilde{G}^*_{zx} \\ &+\tilde{\alpha}_{zy}\tilde{\mathcal{G}}^*_{xx} - \tilde{\alpha}_{zx}\tilde{\mathcal{G}}^*_{yx}) + \frac{1}{3}\omega\mathrm{Re}(\tilde{\alpha}_{zx}\tilde{A}^*_{zzy} \\ &-\tilde{\alpha}_{zy}\tilde{A}^*_{zzx} + \tilde{\alpha}_{zy}\tilde{\mathcal{A}}^*_{xzy} - \tilde{\alpha}_{zx}\tilde{\mathcal{A}}^*_{yzy}) + \cdots] \end{aligned} \tag{1.2d}$$

where we have introduced the complex dynamic molecular property tensors

$$\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} - i\alpha'_{\alpha\beta} \tag{1.3a}$$

$$\tilde{G}_{\alpha\beta} = G_{\alpha\beta} - iG'_{\alpha\beta} \tag{1.3b}$$

$$\tilde{A}_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} - iA'_{\alpha\beta\gamma} \tag{1.3c}$$

$$\tilde{\mathcal{G}}_{\alpha\beta} = G_{\alpha\beta} + iG'_{\alpha\beta} \tag{1.3d}$$

$$\tilde{\mathcal{A}}_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} + iA'_{\alpha\beta\gamma} \tag{1.3e}$$

A complex quantity is denoted by a tilde. Expressions for the real and imaginary parts are provided by time-dependent perturbation theory as follows [1,12,13]:

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\mathrm{Re}(\langle n \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle) \tag{1.4a}$$

$$\alpha'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\mathrm{Im}(\langle n \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle) \tag{1.4b}$$

$$G_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\mathrm{Re}(\langle n \mid \mu_\alpha \mid j\rangle\langle j \mid m_\beta \mid n\rangle) \tag{1.4c}$$

$$G'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\mathrm{Im}(\langle n \mid \mu_\alpha \mid j\rangle\langle j \mid m_\beta \mid n\rangle) \tag{1.4d}$$

$$A_{\alpha\beta\gamma} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\mathrm{Re}(\langle n \mid \mu_\alpha \mid j\rangle\langle j \mid \Theta_{\beta\gamma} \mid n\rangle) \tag{1.4e}$$

$$A'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2-\omega^2}\mathrm{Im}(\langle n \mid \mu_\alpha \mid j\rangle\langle j \mid \Theta_{\beta\gamma} \mid n\rangle) \quad (1.4f)$$

where $\omega_{jn} = \omega_j - \omega_n$, and μ_α, m_α and $\Theta_{\alpha\beta}$ are the electric dipole, magnetic dipole and traceless electric quadrupole moment operators respectively, defined by

$$\mu_\alpha = \sum_i e_i r_{i_\alpha} \quad (1.5a)$$

$$m_\alpha = \sum_i \frac{e_i}{2m_i}\epsilon_{\alpha\beta\gamma} r_{i_\beta} p_{i_\gamma} \quad (1.5b)$$

$$\Theta_{\alpha\beta} = \frac{1}{2}\sum_i e_i(3r_{i_\alpha}r_{i_\beta} - r_i^2\delta_{\alpha\beta}) \quad (1.5c)$$

The summations are over all particles i, with position vector $\mathbf{r}_i$, charge e_i and linear momentum $\mathbf{p}_i$, $\delta_{\alpha\beta}$ is the unit symmetric second-rank tensor and $\epsilon_{\alpha\beta\gamma}$ is the unit antisymmetric third-rank tensor. We have also made use of the Einstein summation convention whereby a repeated Greek suffix implies summation over the Cartesian components [1].

The circular intensity sums and differences may be applied to Raman optical activity by replacing the property tensors by transition tensors, so that, for example, $\tilde{\alpha}_{\alpha\beta}$ becomes $(\tilde{\alpha}_{\alpha\beta})_{mn}$ where $|n\rangle$ and $|m\rangle$ are the initial and final states. The complex transition polarizability and optical activity tensors are given by [1]

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle}{\omega_{jn}-\omega} + \frac{\langle m \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle}{\omega_{jm}+\omega}\right] \quad (1.6a)$$

$$(\tilde{G}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid m_\beta \mid n\rangle}{\omega_{jn}-\omega} + \frac{\langle m \mid m_\beta \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle}{\omega_{jm}+\omega}\right] \quad (1.6b)$$

$$(\tilde{A}_{\alpha\beta\gamma})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid \Theta_{\beta\gamma} \mid n\rangle}{\omega_{jn}-\omega} + \frac{\langle m \mid \Theta_{\beta\gamma} \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle}{\omega_{jm}+\omega}\right] \quad (1.6c)$$

It proves instructive to write these complex transition tensors as a sum of real and imaginary parts as follows:

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = (\alpha_{\alpha\beta})^+_{mn} + (\alpha_{\alpha\beta})^-_{mn} - i(\alpha'_{\alpha\beta})^+_{mn} - i(\alpha'_{\alpha\beta})^-_{mn} \quad (1.7a)$$

where

$$(\alpha_{\alpha\beta})^+_{mn} = \frac{1}{2\hbar}\sum_{j\neq n,m}\frac{(\omega_{jn}+\omega_{jm})}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)} \times \mathrm{Re}(\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle + \langle m \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle) \quad (1.7b)$$

$$(\alpha_{\alpha\beta})^{-}_{mn} = \frac{1}{2\hbar}\sum_{j\neq n,m}\frac{(2\omega+\omega_{nm})}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)} \times \mathrm{Re}(\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle - \langle m \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle) \quad (1.7c)$$

$$(\alpha'_{\alpha\beta})^{+}_{mn} = -\frac{1}{2\hbar}\sum_{j\neq n,m}\frac{(\omega_{jn}+\omega_{jm})}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)} \times \mathrm{Im}(\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle + \langle m \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle) \quad (1.7d)$$

$$(\alpha'_{\alpha\beta})^{-}_{mn} = -\frac{1}{2\hbar}\sum_{j\neq n,m}\frac{(2\omega+\omega_{nm})}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)} \times \mathrm{Im}(\langle m \mid \mu_\alpha \mid j\rangle\langle j \mid \mu_\beta \mid n\rangle - \langle m \mid \mu_\beta \mid j\rangle\langle j \mid \mu_\alpha \mid n\rangle) \quad (1.7e)$$

$(\tilde{G}_{\alpha\beta})_{mn}$ and $(\tilde{A}_{\alpha\beta\gamma})_{mn}$ may be broken down in an analogous fashion. These complex transition tensors have corresponding effective operators [1,14,15].

$$\hat{\alpha}_{\alpha\beta} = \hat{\alpha}^{+}_{\alpha\beta} + \hat{\alpha}^{-}_{\alpha\beta} \quad (1.8a)$$

$$\hat{G}_{\alpha\beta} = \hat{G}^{+}_{\alpha\beta} + \hat{G}^{-}_{\alpha\beta} \quad (1.8b)$$

$$\hat{A}_{\alpha\beta\gamma} = \hat{A}^{+}_{\alpha\beta\gamma} + \hat{A}^{-}_{\alpha\beta\gamma} \quad (1.8c)$$

where

$$\hat{\alpha}^{+}_{\alpha\beta} = \frac{1}{2}(\mu_\alpha O^{+}\mu_\beta + \mu_\beta O^{+}\mu_\alpha) \quad (1.8d)$$

$$\hat{\alpha}^{-}_{\alpha\beta} = -\frac{1}{2}(\mu_\alpha O^{-}\mu_\beta - \mu_\beta O^{-}\mu_\alpha) \quad (1.8e)$$

$$\hat{G}^{+}_{\alpha\beta} = \frac{1}{2}(\mu_\alpha O^{+}m_\beta + m_\beta O^{+}\mu_\alpha) \quad (1.8f)$$

$$\hat{G}^{-}_{\alpha\beta} = -\frac{1}{2}(\mu_\alpha O^{-}m_\beta - m_\beta O^{-}\mu_\alpha) \quad (1.8g)$$

$$\hat{A}^{+}_{\alpha\beta\gamma} = \frac{1}{2}(\mu_\alpha O^{+}\Theta_{\beta\gamma} + \Theta_{\beta\gamma}O^{+}\mu_\alpha) \quad (1.8h)$$

$$\hat{A}^{-}_{\alpha\beta\gamma} = -\frac{1}{2}(\mu_\alpha O^{-}\Theta_{\beta\gamma} - \Theta_{\beta\gamma}O^{-}\mu_\alpha) \quad (1.8i)$$

$$O^{\pm} = \left(\frac{1}{H-\overline{E}+\hbar\omega} \pm \frac{1}{H-\overline{E}-\hbar\omega}\right) \quad (1.8j)$$

and $\overline{E}$ is the average of the energies E_n and E_m of the initial and final states.

The complex transition tensors may be generated by taking matrix elements of the effective operators, summing over a complete set of states $|j\rangle\langle j|$ inserted after

$O^{\pm}$ and using the approximation $\omega_{jn} \approx \omega_{jm}$. Writing the effective operators in the form (1.8) allows us to deduce the symmetry properties of each operator from those of its component parts [1,14,15].

Thus we find that $\hat{\alpha}^{+}_{\alpha\beta}$ is Hermitian, has even parity and is time-even, $\hat{\alpha}^{-}_{\alpha\beta}$ is anti-Hermitian, has even parity and is time-odd, $\hat{G}^{+}_{\alpha\beta}$ is Hermitian, has odd parity and is time-odd, $\hat{G}^{-}_{\alpha\beta}$ is anti-Hermitian, has odd parity and is time-even, $\hat{A}^{+}_{\alpha\beta\gamma}$ is Hermitian, has odd parity and is time-even and $\hat{A}^{-}_{\alpha\beta\gamma}$ is anti-Hermitian, has odd parity, and is time-odd. Using these properties with the result

$$\langle \Theta n \mid \hat{S}(\pm) \mid \Theta m \rangle = \pm \langle m \mid \hat{S}(\pm) \mid n \rangle \tag{1.9}$$

where Θ is the quantum mechanical time-reversal operator, $\hat{S}$ is an arbitrary operator and the bracketed sign indicates the behaviour of $\hat{S}$ under time-reversal, we deduce that [1,14,15]

$$\langle m \mid \hat{\alpha}_{\alpha\beta} \mid n \rangle = \langle \Theta n \mid \hat{\alpha}_{\beta\alpha} \mid \Theta m \rangle = \langle \Theta m \mid \hat{\alpha}_{\alpha\beta} \mid \Theta n \rangle^{*} \tag{1.10a}$$

$$\langle m \mid \hat{G}_{\alpha\beta} \mid n \rangle = -\langle \Theta m \mid \hat{G}_{\alpha\beta} \mid \Theta n \rangle^{*} \tag{1.10b}$$

$$\langle m \mid \hat{A}_{\alpha\beta\gamma} \mid n \rangle = \langle \Theta m \mid \hat{A}_{\alpha\beta\gamma} \mid \Theta n \rangle^{*} \tag{1.10c}$$

For an even-electron system, in the absence of a time-odd influence, the initial and final states can be chosen to be either even or odd with respect to time reversal and it follows that only the real parts of $\langle m \mid \hat{\alpha}_{\alpha\beta} \mid n \rangle$ and $\langle m \mid \hat{A}_{\alpha\beta\gamma} \mid n \rangle$ and imaginary part of $\langle m \mid \hat{G}_{\alpha\beta} \mid n \rangle$ may be non-zero. An odd-electron system requires a more involved treatment and we shall not consider it here.

The conventional Raman effect is associated with nuclear motions for which the characteristic frequencies are significantly less than either the frequency of electronic transitions or the frequency of the incident radiation. If we impose the further condition that the incident light is far from any absorption frequency, it becomes possible to introduce approximations to simplify the form of $(\alpha_{\alpha\beta})_{mn}$. In order to realise this simplification the Born-Oppenheimer approximation is invoked in addition to a separation of vibrational and rotational motion. This allows a general

molecular wavefunction $|j\rangle$ to be written as the product of an electronic wavefunction $|j_e\rangle$, a vibrational wavefunction $|j_v\rangle$ and a rotational wavefunction $|j_r\rangle$. Then, the rotational and vibrational contributions to the transition frequencies in the polarizability are neglected and we make use of closure to sum over the complete set of rovibrational states associated with an electronic state. If it is also assumed that the molecule is in a quantum state belonging to the lowest electronic level such that $n_e = m_e = 0$ and the adiabatic dynamic polarizability is introduced

$$\begin{aligned} \alpha_{\alpha\beta}(Q) &= \frac{2}{\hbar} \sum_{j_e \neq 0} \frac{\omega_{j e^\circ}}{\omega_{j_{e^\circ}}^2 - \omega^2} \\ &\quad \times \mathrm{Re}(\langle 0 \mid \mu_\alpha(r,Q) \mid j_e \rangle \langle j_e \mid \mu_\beta(r,Q) \mid 0 \rangle) \end{aligned} \tag{1.11}$$

where r and Q are electronic and nuclear co-ordinates respectively, then it is possible to write [16,17]

$$(\alpha_{\alpha\beta})_{mn} = (\alpha_{\alpha\beta})_{m_e m_v m_r, n_e n_v n_r} = \langle m_v m_r \mid \alpha_{\alpha\beta}(Q) \mid n_v n_r \rangle \tag{1.12}$$

It should be noted that these assumptions and attendant simplifications, which constitute what is usually called Placzek's approximation, when taken in conjunction with time-reversal arguments, dictate that only $(\alpha_{\alpha\beta})^+_{mn}$ of the original complex matrix element $(\tilde{\alpha}_{\alpha\beta})_{mn}$ survives for an even-electron molecule in a non-degenerate state. Similar developments are available for the optical activity tensors showing that only $(G'_{\alpha\beta})^-_{mn}$ and $(A_{\alpha\beta\gamma})^+_{mn}$ survive [1,14,15].

From the definition of $(\alpha_{\alpha\beta})^+_{mn}$ given by (1.7b) it is obvious that $(\alpha_{\alpha\beta})^+_{mn} = (\alpha_{\beta\alpha})^+_{mn}$ and thus scattering generated by this matrix element is often called symmetric. Placzek's approximation breaks down under resonance conditions, for electronic Raman scattering and in the presence of degeneracy. Any of these factors either separately or in combination may allow an antisymmetric scattering contribution to a particular band [18]. Antisymmetric scattering has, for example, been observed in the vibrational bands of resonance vibrational Raman spectra of haem proteins [19] and iridium (IV) hexahalides [20]. Although resonance Raman spectra of gaseous samples showing rotational structure have been recorded and interpreted

[21,22], no molecule which is a potential antisymmetric scatterer by virtue of its possession of electronic angular momentum seems to have been chosen for this type of study. Nevertheless, there are many potential candidates for an investigation of antisymmetric scattering in resonance rotational or rovibrational Raman spectra. A simple example would be the nitric oxide molecule with the impinging beam in resonance with one of the so-called β bands associated with the $A^2\Pi \leftarrow X^2\Pi$ electronic transition [23]. It is interesting to note that Ziegler has observed antisymmetric UV-resonance Raman scattering with degeneracy in the rotational states [24].

The rotational selection rules for antisymmetric scattering are not a function of molecular symmetry alone. These rules depend on the appropriate set of angular momentum quantum numbers for specification of the molecular state, and this in turn requires determination of which mode of coupling, and thus Hund's case, is relevant [23,25]. A rigorous theoretical treatment of rotational antisymmetric scattering is not a trivial undertaking and no attempt is made to include the possibility of scattering of this type in the following development.

1.2.2 Intensity factors

We shall work exclusively within the limitations of Placzek's approximation and the appropriate positive or negative superscript associated with a polarizability or optical activity tensor component will be taken as understood. Since we are interested in rotational Raman scattering, we develop (1.12) further by transforming from space-fixed to molecule-fixed axes, so that the rotational transitions are effected by the direction cosines relating the axes systems:

$$\langle m_v m_r \mid \alpha_{\alpha\beta}(Q) \mid n_v n_r \rangle = (\alpha_{\alpha'\beta'}(Q))_{m_v n_v} \langle m_r \mid \ell_{\alpha\alpha'} \ell_{\beta\beta'} \mid n_r \rangle \qquad (1.13)$$

However, derivations are facilitated by replacing the conventional direction cosine formalism by the irreducible spherical tensor formalism [26-29]. An appendix giv-

ing a short introduction to this method and relating irreducible spherical tensor components to Cartesian components has been provided.

In Placzek and Teller's original work on rotational Raman scattering intensities [30], circular tensor components were introduced as a first step towards establishing a natural basis for the expression of rotational line strengths. Using spherical tensors allows, in addition, exploitation of the properties of both the $3-j$ symbols and the transformation matrices relating space and molecule-fixed spherical components [29,31]. The intensity of a Raman line in the absence of an external magnetic field is proportional to quantities of the form [32]

$$\sum_{MM'} |\langle n', J'K'M' \mid \hat{\alpha}_q^k \mid n, JKM\rangle|^2 \tag{1.14}$$

where $\hat{\alpha}_q^k$ is the qth component of the rank k set of polarizability tensor operators. The rotational states are characterised by quantum numbers J, K and M where J specifies the total angular momentum of the nuclear framework, with K and M specifing its projection on molecule-fixed and space-fixed axes respectively. The vibrational states are characterised by n. For symmetric isotropic and anisotropic scattering k takes the values of zero and two respectively. Contributing values of q are determined by the characteristics of the impinging beam and the chosen experimental arrangement for intensity measurements on the scattered light.

It is necessary to generalise in order to take account of scattering generated by the optical activity tensor operators $\hat{\mathbf{G}}$ and $\hat{\mathbf{A}}$, and to allow for interference terms $\hat{\boldsymbol{\alpha}}\,\hat{\mathbf{G}}$ and $\hat{\boldsymbol{\alpha}}\,\hat{\mathbf{A}}$. Thus for a rovibrational transition $n', J'K'M' \longleftarrow n, JKM$ we define an intensity factor corresponding to a $\hat{\mathbf{T}}\hat{\mathbf{S}}$ scattering contributions

$$\begin{aligned}[I_q^k(TS)]_{n'J'K',nJK} &= \frac{1}{(2J+1)} \sum_{MM'} \langle n', J'K'M' \mid \hat{T}_q^k \mid n, JKM\rangle \\ &\quad \times \langle n', J'K'M' \mid \hat{S}_q^k \mid n, JKM\rangle^* \end{aligned} \tag{1.15}$$

Note that we have made use of the fact that each of the $2J+1$ values of M in the initial state is equally probable. Our concern lies with conventional symmetric scattering and the associated discriminatory contributions ($k = 0, 2$). The general

formalism with $k = 1$ could easily be adapted to treat electric dipole absorption probabilities in microwave spectroscopy.

An extension of the Wigner-Eckart theorem to axially symmetric systems allows expression of symmetric top matrix elements in terms of $3-j$ symbols [33,34]:

$$\begin{aligned}\langle n', J'K'M' \mid \hat{T}^k_q \mid n, JKM\rangle &= i^{J'+J-K'-K}(-1)^{J'-M'}[(2J'+1)(2J+1)]^{\frac{1}{2}} \\ &\times \begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}\begin{pmatrix} J' & k & J \\ -M' & q & M \end{pmatrix} \\ &\times \langle n' \mid \overline{\hat{T}^k_{K'-K}} \mid n\rangle \end{aligned} \tag{1.16}$$

where a bar over the operator indicates molecule-fixed axes. Then (1.16) may be inserted into (1.15) to obtain

$$\begin{aligned}[I^k_q(TS)]_{n'J'K',nJK} &= \frac{(2J'+1)}{(2k+1)}\begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}^2 \\ &\times \langle n' \mid \overline{\hat{T}^k_{K'-K}} \mid n\rangle\langle n' \mid \overline{\hat{S}^k_{K'-K}} \mid n\rangle^* \end{aligned} \tag{1.17}$$

Introducing

$$D^k_{J'K',JK} = (2J'+1)\begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}^2 \tag{1.18}$$

allows (1.17) to be written more simply as

$$[I^k_q(TS)]_{n'J'K',nJK} = \frac{1}{(2k+1)}\langle n' \mid \overline{\hat{T}^k_{K'-K}} \mid n\rangle\langle n' \mid \overline{\hat{S}^k_{K'-K}} \mid n\rangle^* D^k_{J'K',JK} \tag{1.19}$$

Our general treatment may be seen to be consistent with the earlier literature on rotational Raman scattering by noting that the factor $D^k_{J'K',JK}$ is identical to the Placzek-Teller factor $b^{JK}_{J'K'}$ when $k = 2$. The relations between the factors $b^{JK}_{J'K'}$ as presented by Gaufres and Sportouch [35] follow immediately from the symmetry properties of the $3-j$ symbols. We reproduce these results in more general form in terms of $D^k_{J'K',JK}$:

$$D^k_{J'K',JK} = D^k_{J'-K',J-K} \tag{1.20a}$$

$$(2J+1)D^k_{J'K',JK} = (2J'+1)D^k_{JK,J'K'} \quad (1.20b)$$

$$\sum_{J'} D^k_{J'K',JK} = 1 \quad (1.20c)$$

$$\sum_{K} D^k_{J'K',JK} = \sum_{K'} D^k_{J'K',JK} = (2J'+1)/(2k+1) \quad (\text{for fixed } \Delta K = K' - K) \quad (1.20d)$$

Relation (1.20a) depends on the fact that the square of a $3-j$ symbol does not change when the signs of the second row numbers are reversed and (1.20b) follows from the fact that the square of a $3-j$ symbol does not change when two of its columns are interchanged. Relations (1.20c) and (1.20d) are a consequence of the orthogonality of $3-j$ symbols.

1.2.3 Selection rules

Rotational selection rules for rotation-vibration Raman scattering depend on the conditions required for the $3-j$ symbols in (1.19) to be non-zero. For k=2 these are

$$\Delta J = 0, \pm 1, \pm 2 \quad (1.21a)$$

$$\Delta K = 0, \pm 1, \pm 2 \quad (1.21b)$$

while for $k = 0$ we have

$$\Delta J = \Delta K = 0 \quad (1.21c)$$

This is the most general case, but further restrictions on ΔK are placed on molecules in possession of symmetry elements, since a given vibrational transition may then only be effected by selected component operators $\overline{\hat{\alpha}^k_{K-K'}}$. We note that the only symmetric polarizability operator components which transform as the totally symmetric representation of the symmetric top point groups are

$$\overline{\hat{\alpha}^o_o} = -\sqrt{3}\hat{\alpha} \quad (1.22a)$$

$$\overline{\hat{\alpha}_o^2} = \frac{2}{\sqrt{6}}(\hat{\alpha}_{||} - \hat{\alpha}_{\perp}) \tag{1.22b}$$

where $\alpha = \frac{1}{3}\alpha_{\alpha\alpha}$ is the mean polarizability, $\alpha_{||} = \alpha_{ZZ}$ and $\alpha_{\perp} = \alpha_{XX} = \alpha_{YY}$. X, Y and Z denote the molecule-fixed principal axes. Thus for pure rotational scattering and vibration-rotation scattering in fundamentals of totally symmetric modes only $\Delta K = 0$ occurs, while for non-totally symmetric fundamentals only $\Delta K = \pm 1$ and $\Delta K = \pm 2$, or both, occur. The selection rules for vibration-rotation ROA follow from those given for conventional vibration-rotation Raman scattering, since the rotational part of an intensity factor does not depend on the physical nature of the associated tensor operators. However, in addition, the molecule must be chiral in order that the same components of polar and axial tensor operators $\overline{\hat{\alpha}^k_{K-K'}}$ and $\overline{\hat{G}^k_{K-K'}}$ as specified by (1.19) transform identically [1]. The selection rules on rovibrational Raman transitions for chiral symmetric tops are summarized in table 1.1 which is adapted from the standard table of vibration-rotation Raman selection rules given by Stoicheff [36].

To calculate absolute intensities for symmetric scattering, we require the factors $D^k_{J'K',JK}$ with $k = 0, 2$ in explicit algebraic form. These can be obtained by making use of the standard formulae which are available for some of the more common $3-j$ symbols [27]. From the non-vanishing properties of these symbols, it is obvious that for $k = 0$ only $D^0_{JK,JK} = 1$ is allowed. For k=2 the factors are given in table 1.2 and are identical to the previously tabulated expressions for $b^{JK}_{J'K'}$ [30]. Fortunately, we are primarily interested in dimensionless CIDs, for which it will be seen that there is a cancellation of $D^k_{J'K',JK}$ factors in the numerator and denominator in most cases.

1.2.4 Vibration-rotation Raman optical activity

To develop the dimensionless CIDs for rovibrational transitions, the products of Cartesian tensor operator components in (1.2) must be transformed into irreducible spherical tensor operator form. Using the relations listed in the appendix and

Table 1.1

Selection rules for rovibrational Raman transitions in chiral symmetric tops.

Vibrational species	Non-zero components of polarizability and optical activity tensors		Selection rules
	Cartesian components	Spherical components	
totally symmetric	$\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}$	α_0^0	$\Delta J=\Delta K=0$
	$G'_{XX}+G'_{YY}+G'_{ZZ}$	$G_0'^0$	
	$2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY})$	α_0^2	$\Delta J=0,\pm1,\pm2;\ \Delta K=0$
	$2G'_{ZZ}-(G'_{XX}+G'_{YY})$	$G_0'^2$	
	$A_{XYZ}-A_{YZX}$	A_0^2	
non-totally symmetric	$\alpha_{XX}-\alpha_{YY}\pm i(\alpha_{YX}+\alpha_{XY})$	$\alpha_{\pm2}^2$	$\Delta J=0,\pm1,\pm2\ ;\ \Delta K=\pm2$
	$G'_{XX}-G'_{YY}\pm i(G'_{YX}+G'_{XY})$	$G_{\pm2}'^2$	
	$A_{XXZ}-A_{ZXX}+A_{ZYY}-A_{YYZ}$	$A_{\pm2}^2$	
	$\mp i(2A_{ZXY}-A_{XYZ}-A_{YZX})$		
	$\alpha_{XZ}+\alpha_{ZX}\pm i(\alpha_{YZ}+\alpha_{ZY})$	$\alpha_{\pm1}^2$	$\Delta J=0,\pm1,\pm2\ ;\ \Delta K=\pm1$
	$G'_{XZ}+G'_{ZX}\pm i(G'_{YZ}+G'_{ZY})$	$G_{\pm1}'^2$	
	$A_{ZZX}-A_{XZZ}+A_{XYY}-A_{YYX}$	$A_{\pm1}^2$	
	$\pm i(A_{ZZY}-A_{YZZ}+A_{YXX}-A_{XXY})$		

Table 1.2

Rotational Raman factors $D^2_{J'K',JK}$

	J'		
K'	$J-2$	$J-1$	J
$K-2$	$\frac{(J+K)(J+K-1)(J+K-2)(J+K-3)}{4J(J-1)(2J+1)(2J-1)}$	$\frac{(J+K)(J+K-2)[J^2+(K-1)^2]}{2J(J+1)(J-1)(2J+1)}$	$\frac{3[J^2-(K-1)^2][(J+1)^2-(K-1)^2]}{2J(J+1)(2J-1)(2J+3)}$
$K-1$	$\frac{(J^2-K^2)(J+K-1)(J+K-2)}{J(J-1)(2J+1)(2J-1)}$	$\frac{(J+K)(J+K-1)(J-2K+1)^2}{2J(J+1)(J-1)(2J+1)}$	$\frac{3(2K-1)^2(J+K)(J-K+1)}{2J(J+1)(2J-1)(2J+3)}$
K	$\frac{3(J^2-K^2)[(J-1)^2-K^2]}{2J(J-1)(2J+1)(2J-1)}$	$\frac{3K^2(J^2-K^2)}{J(J+1)(J-1)(2J+1)}$	$\frac{[J(J+1)-3K^2]^2}{J(J+1)(2J-1)(2J+3)}$
$K+1$	$\frac{(J^2-K^2)(J-K-1)(J-K-2)}{J(J-1)(2J+1)(2J-1)}$	$\frac{(J-K)(J-K-1)(J+2K+1)^2}{2J(J+1)(J-1)(2J+1)}$	$\frac{3(2K+1)^2(J-K)(J+K+1)}{2J(J+1)(2J-1)(2J+3)}$
$K+2$	$\frac{(J-K)(J-K-1)(J-K-2)(J-K-3)}{4J(J-1)(2J+1)(2J-1)}$	$\frac{(J-K)(J-K-2)[J^2-(K+1)^2]}{2J(J+1)(J-1)(2J+1)}$	$\frac{3[J^2-(K+1)^2][(J+1)^2-(K+1)^2]}{2J(J+1)(2J-1)(2J+3)}$

	J'	
K'	$J+1$	$J+2$
$K-2$	$\frac{[(J+1)^2-(K-1)^2](J-K+1)(J-K+3)}{2J(J+1)(J+2)(2J+1)}$	$\frac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$
$K-1$	$\frac{(J+2K)^2(J-K+1)(J-K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
K	$\frac{3K^2[(J+1)^2-K^2]}{J(J+1)(J+2)(2J+1)}$	$\frac{3[(J+1)^2-K^2][(J+2)^2-K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$
$K+1$	$\frac{(J-2K)^2(J+K+1)(J+K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$K+2$	$\frac{[(J+1)^2-(K+1)^2](J+K+1)(J+K+3)}{2J(J+1)(J+2)(2J+1)}$	$\frac{(J+K+1)(J+K+2)(J+K+3)(J+K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$

neglecting antisymmetric scattering contributions, we obtain

$$\tilde{\alpha}_{xx}\tilde{G}^*_{xx} \rightarrow \frac{1}{12}(4\hat{\alpha}^o_o\hat{G}^{o*}_o + 2\hat{\alpha}^2_o\hat{G}^{2*}_o + 3\hat{\alpha}^2_2\hat{G}^{2*}_2 + 3\hat{\alpha}^2_{-2}\hat{G}^{2*}_{-2}) \quad (1.23a)$$

$$\tilde{\alpha}_{xy}\tilde{G}^*_{xy} \rightarrow \frac{1}{4}(\hat{\alpha}^2_2\hat{G}^{2*}_2 + \hat{\alpha}^2_{-2}\hat{G}^{2*}_{-2}) \quad (1.23b)$$

$$\tilde{\alpha}_{zx}\tilde{G}^*_{zx} \rightarrow \frac{1}{4}(\hat{\alpha}^2_1\hat{G}^{2*}_1 + \hat{\alpha}^2_{-1}\hat{G}^{2*}_{-1}) \quad (1.23c)$$

$$\tilde{\alpha}_{zy}\tilde{G}^*_{zy} \rightarrow \frac{1}{4}(\hat{\alpha}^2_1\hat{G}^{2*}_1 + \hat{\alpha}^2_{-1}\hat{G}^{2*}_{-1}) \quad (1.23d)$$

$$\tilde{\alpha}_{xx}\tilde{A}^*_{xyz} \rightarrow -\frac{i}{4\sqrt{6}}(2\hat{\alpha}^2_o\hat{A}^{2*}_o - \hat{\alpha}^2_2\hat{A}^{2^*}_2 - \hat{\alpha}^2_{-2}\hat{A}^{2*}_{-2}) \quad (1.23e)$$

$$\tilde{\alpha}_{xy}\tilde{A}^*_{xxz} \rightarrow -\frac{i}{4\sqrt{6}}(\hat{\alpha}^2_2\hat{A}^{2*}_2 + \hat{\alpha}^2_{-2}\hat{A}^{2*}_{-2}) \quad (1.23f)$$

$$\tilde{\alpha}_{zx}\tilde{A}^*_{zzy} \rightarrow -\frac{i}{4\sqrt{6}}(\hat{\alpha}^2_1\hat{A}^{2*}_1 + \hat{\alpha}^2_{-1}\hat{A}^{2*}_{-1}) \quad (1.23g)$$

$$\tilde{\alpha}_{zy}\tilde{A}^*_{zzx} \rightarrow \frac{i}{4\sqrt{6}}(\hat{\alpha}^2_1\hat{A}^{2*}_1 + \hat{\alpha}^2_{-1}\hat{A}^{2*}_{-1}) \quad (1.23h)$$

In the circular intensity sums, $\tilde{\alpha}_{xx}\tilde{\alpha}^*_{xx}$, $\tilde{\alpha}_{xy}\tilde{\alpha}^*_{xy}$, $\tilde{\alpha}_{zx}\tilde{\alpha}^*_{zx}$ and $\tilde{\alpha}_{zy}\tilde{\alpha}^*_{zy}$ transform analogously to (1.23a)-(1.23d) with $\tilde{\alpha}$ replacing $\tilde{G}$. Each term $\hat{T}^k_q\hat{S}^{k^*}_q$ is then correlated with an intensity factor $[I^k_q(TS)]_{n'J'K',nJK}$ defined by (1.19).

We thus may construct tables 1.3a and 1.3b in which for conciseness we have suppressed the full matrix element notation, so that $\alpha_{\alpha\beta}$ is understood to mean $(\alpha_{\alpha\beta})_{n'n}$ and similarly for the optical activity tensor matrix elements. Using tables 1.3a and 1.3b we can write down the polarized and depolarized dimensionless CIDs Δ_x and Δ_z associated with allowed vibration-rotation transitions.

(a) Totally symmetric modes of vibration:

$\Delta J = 0$, $\Delta K = 0$

(For pure rotational scattering, this constitutes the Rayleigh line)

$$\Delta_x = \frac{2}{c}\left\{45\alpha G' + \frac{[3K^2 - J(J+1)]^2(\alpha_{||} - \alpha_\perp)}{J(J+1)(2J+3)(2J-1)}\left[7(G'_{||} - G'_\perp) + \omega A_{XYZ}\right]\right\} \times \left\{45\alpha^2 + \frac{7[3K^2 - J(J+1)]^2}{J(J+1)(2J+3)(2J-1)}(\alpha_{||} - \alpha_\perp)^2\right\}^{-1} \quad (1.24a)$$

$$\Delta_z = \frac{2\left[(G'_{||} - G'_\perp) - \frac{1}{3}\omega A_{XYZ}\right]}{c(\alpha_{||} - \alpha_\perp)} \quad (1.24b)$$

Table 1.3a

CIDs for rovibrational transitions in symmetric tops.

	$\mathrm{Im}(\tilde{\alpha}_{xx}\tilde{G}^*_{xx} + \tilde{\alpha}_{xy}\tilde{G}^*_{xy})$	$\mathrm{Im}(\tilde{\alpha}_{zx}\tilde{G}^*_{zx} + \tilde{\alpha}_{zy}\tilde{G}^*_{zy})$
ΔK		
0	$\frac{1}{45}[7(\alpha_{\parallel} - \alpha_{\perp})(G'_{\parallel} - G'_{\perp})D^2_{J'K,JK}$ $+45\alpha G' D^0_{JK,JK}]$	$\frac{2}{15}(\alpha_{\parallel} - \alpha_{\perp})(G'_{\parallel} - G'_{\perp})D^2_{J'K,JK}$
± 1	$\frac{7}{60}[\alpha_{XZ}(G'_{XZ} + G'_{ZX})$ $+\alpha_{YZ}(G'_{YZ} + G'_{ZY})]D^2_{J'K\pm1,JK}$	$\frac{1}{10}[\alpha_{XZ}(G'_{XZ} + G'_{ZX})$ $+\alpha_{YZ}(G'_{YZ} + G'_{ZY})]D^2_{J'K\pm1,JK}$
± 2	$\frac{7}{120}[(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY})$ $+2\alpha_{XY}(G'_{XY} + G'_{YX})]D^2_{J'K\pm2,JK}$	$\frac{1}{20}[(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY})$ $+2\alpha_{XY}(G'_{XY} + G'_{YX})]D^2_{J'K\pm2,JK}$

Table 1.3b

CIDs for rovibrational transitions in symmetric tops.

	$\frac{1}{3}\omega\mathrm{Re}(\tilde{\alpha}_{xx}\tilde{A}^*_{xyz} - \tilde{\alpha}_{xy}\tilde{A}^*_{xxz})$	$\frac{1}{3}\omega\mathrm{Re}(\tilde{\alpha}_{zx}\tilde{A}^*_{zzy} - \tilde{\alpha}_{zy}\tilde{A}^*_{xxz})$
ΔK		
0	$\frac{1}{45}\omega(\alpha_{\parallel} - \alpha_{\perp})A_{XYZ}D^2_{J'K,JK}$	$-\frac{2}{45}\omega(\alpha_{\parallel} - \alpha_{\perp})A_{XYZ}D^2_{J'K,JK}$
±1	$\frac{1}{180}\omega[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX})$ $-\alpha_{XZ}(A_{ZZY} - A_{YZZ} + A_{YXX} - A_{XXY})]D^2_{J'K\pm1,JK}$	$-\frac{1}{90}\omega[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX})$ $-\alpha_{XZ}(A_{ZZY} - A_{YZZ} + A_{YXX} - A_{XXY})]D^2_{J'K\pm1,JK}$
±2	$\frac{1}{360}\omega[(\alpha_{XX} - \alpha_{YY})(A_{XYZ} + A_{YZX} - 2A_{ZXY})$ $+2\alpha_{XY}(A_{ZXX} - A_{XXZ} + A_{YYZ} - A_{ZYY})]D^2_{J'K\pm2,JK}$	$-\frac{1}{180}\omega[(\alpha_{XX} - \alpha_{YY})(A_{XYZ} + A_{YZX} - 2A_{ZXY})$ $+2\alpha_{XY}(A_{ZXX} - A_{XXZ} + A_{YYZ} - A_{ZYY})]D^2_{J'K\pm2,JK}$

$\Delta J = \pm 1, \pm 2,\ \Delta K = 0$

$$\Delta_x = \frac{2\left[7(G'_{\|} - G'_{\perp}) + \omega A_{XYZ}\right]}{7c(\alpha_{\|} - \alpha_{\perp})} \tag{1.25a}$$

$$\Delta_z = \frac{2\left[(G'_{\|} - G'_{\perp}) - \frac{1}{3}\omega A_{XYZ}\right]}{c(\alpha_{\|} - \alpha_{\perp})} \tag{1.25b}$$

(b) Non-totally symmetric modes of vibration:

$\Delta J = 0, \pm 1, \pm 2,\ \Delta K = \pm 1$

$$\begin{aligned}\Delta_x &= \frac{1}{c}\Big[\alpha_{XZ}(G'_{XZ} + G'_{ZX}) + \alpha_{YZ}(G'_{YZ} + G'_{ZY}) \\ &\quad + \frac{1}{21}\omega[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX}) \\ &\quad - \alpha_{XZ}(A_{ZZY} - A_{YZZ} + A_{YXX} - A_{XXY})]\Big] \\ &\quad \times(\alpha_{XZ}^2 + \alpha_{YZ}^2)^{-1}\end{aligned} \tag{1.26a}$$

$$\begin{aligned}\Delta_z &= \frac{1}{c}\Big[\alpha_{XZ}(G'_{XZ} + G'_{ZX}) + \alpha_{YZ}(G'_{YZ} + G'_{ZY}) \\ &\quad - \frac{1}{9}\omega[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX}) \\ &\quad - \alpha_{XZ}(A_{ZZY} - A_{YZZ} + A_{YXX} - A_{XXY})]\Big] \\ &\quad \times(\alpha_{XZ}^2 + \alpha_{YZ}^2)^{-1}\end{aligned} \tag{1.26b}$$

$\Delta J = 0, \pm 1, \pm 2, \Delta K = \pm 2$

$$\begin{aligned}\Delta_x &= \frac{2}{c}\Big[(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY}) + 2\alpha_{XY}(G'_{XY} + G'_{YX}) \\ &\quad - \frac{1}{21}\omega[(\alpha_{XX} - \alpha_{YY})(2A_{ZXY} - A_{XYZ} - A_{YZX}) \\ &\quad + 2\alpha_{XY}(A_{XXZ} - A_{ZXX} + A_{ZYY} - A_{YYZ})]\Big] \\ &\quad \times[(\alpha_{XX} - \alpha_{YY})^2 + 4\alpha_{XY}^2]^{-1}\end{aligned} \tag{1.27a}$$

$$\begin{aligned}\Delta_z &= \frac{2}{c}\Big[(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY}) + 2\alpha_{XY}(G'_{XY} + G'_{YX}) \\ &\quad + \frac{1}{9}\omega[(\alpha_{XX} - \alpha_{YY})(2A_{ZXY} - A_{XYZ} - A_{YZX}) \\ &\quad + 2\alpha_{XY}(A_{XXZ} - A_{ZXX} + A_{ZYY} - A_{YYZ})]\Big] \\ &\quad \times[(\alpha_{XX} - \alpha_{YY})^2 + 4\alpha_{XY}^2]^{-1}\end{aligned} \tag{1.27b}$$

Having determined the CIDs for all possible cases of individual rovibrational transitions, we continue by considering the total unresolved CID for the envelope of bands associated with vibrational transition $n' \leftarrow n$. For each initial rotational state j, it is necessary to sum over the intensity factors of all allowed final states j' and then to take the Boltzmann average of the resulting expression $X^{(j)}$ over all possible initial states j using

$$\overline{X} = \frac{\sum_j g_j X^{(j)} e^{-E_j/kT}}{\sum_j g_j e^{-E_j/kT}} \tag{1.28}$$

where g_j is the degeneracy of state j. However, since ΔK is fixed for each intensity factor, summation over all final states may be effected with the use of (1.20c) to give a value for X which is independent of rotational state. The Boltzmann average over initial states is thus trivial.

The unresolved dimensionless CIDs for totally symmetric modes of vibration ($\Delta K = 0$) are found to be

$$\Delta_x = \frac{2[45\alpha G' + 7(\alpha_{\|} - \alpha_{\perp})(G'_{\|} - G'_{\perp}) + \omega(\alpha_{\|} - \alpha_{\perp})A_{XYZ}]}{c[45\alpha^2 + 7(\alpha_{\|} - \alpha_{\perp})^2]} \tag{1.29a}$$

$$\Delta_z = \frac{2[(G'_{\|} - G'_{\perp}) - \frac{1}{3}\omega A_{XYZ}]}{c(\alpha_{\|} - \alpha_{\perp})} \tag{1.29b}$$

For non-totally symmetric modes of vibration with exclusively $\Delta K = \pm 1$ or ± 2 allowed, the unresolved dimensionless CIDs are identical to the CIDs for individual transitions given by (1.26) and (1.27), while, for vibrational modes for which both $\Delta K = \pm 1$ and $\Delta K = \pm 2$ are permitted, we obtain

$$\begin{aligned}
\Delta_x = {} & \frac{1}{c}\Big\{\alpha_{XZ}(G'_{XZ} + G'_{ZX}) + \alpha_{YZ}(G'_{YZ} + G'_{ZY}) + \alpha_{XY}(G'_{XY} + G'_{YX}) \\
& + \frac{1}{2}(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY}) + \frac{1}{21}\omega[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX}) \\
& + \alpha_{XZ}(A_{YZZ} - A_{ZZY} + A_{XXY} - A_{YXX}) \\
& + \alpha_{XY}(A_{ZXX} - A_{XXZ} + A_{YYZ} - A_{ZYY}) \\
& - \frac{1}{2}(\alpha_{XX} - \alpha_{YY})(2A_{ZXY} - A_{XYZ} - A_{YZX})]\Big\} \\
& \times \left\{\alpha_{XZ}^2 + \alpha_{YZ}^2 + \alpha_{XY}^2 + \frac{1}{4}(\alpha_{XX} - \alpha_{YY})^2\right\}^{-1}
\end{aligned} \tag{1.30a}$$

$$\Delta_z = \frac{1}{c}\Big\{\alpha_{XZ}(G'_{XZ}+G'_{ZX})+\alpha_{YZ}(G'_{YZ}+G'_{ZY})+\alpha_{XY}(G'_{XY}+G'_{YX})$$
$$+\frac{1}{2}(\alpha_{XX}-\alpha_{YY})(G'_{XX}-G'_{YY})-\frac{1}{9}\omega[\alpha_{YZ}(A_{ZZX}-A_{XZZ}+A_{XYY}-A_{YYX})$$
$$+\alpha_{XZ}(A_{YZZ}-A_{ZZY}+A_{XXY}-A_{YXX})$$
$$+\alpha_{XY}(A_{ZXX}-A_{XXZ}+A_{YYZ}-A_{ZYY})$$
$$-\frac{1}{2}(\alpha_{XX}-\alpha_{YY})(2A_{ZXY}-A_{XYZ}-A_{YZX})]\Big\}$$
$$\times\Big\{\alpha^2_{XZ}+\alpha^2_{YZ}+\alpha^2_{XY}+\frac{1}{4}(\alpha_{XX}-\alpha_{YY})^2\Big\}^{-1} \qquad (1.30b)$$

As noted in the introduction, these unresolved CIDs should be consistent with the CIDs for vibrational Raman scattering from an isotropic fluid calculated by averaging (1.2) over all orientations of the molecule.

For Rayleigh scattering, the isotropic averages of the dimensionless CIDs have been shown to be [1,12]

$$\Delta_x = \frac{2(7\alpha_{\alpha\beta}G'_{\alpha\beta}+\alpha_{\alpha\alpha}G'_{\beta\beta}+\frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(7\alpha_{\lambda\mu}\alpha_{\lambda\mu}+\alpha_{\lambda\lambda}\alpha_{\mu\mu})} \qquad (1.31a)$$

$$\Delta_z = \frac{2(3\alpha_{\alpha\beta}G'_{\alpha\beta}-\alpha_{\alpha\alpha}G'_{\beta\beta}-\frac{1}{3}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta})}{c(3\alpha_{\lambda\mu}\alpha_{\lambda\mu}-\alpha_{\lambda\lambda}\alpha_{\mu\mu})} \qquad (1.31b)$$

Expressions (1.31) also apply to vibrational Raman scattering if the property tensors are replaced by transition tensors, and reduce to (1.26), (1.27), (1.29) and (1.30) for the specified vibrational transition types. To establish this, (1.31) should be written in full, retaining only those transition elements which are non-zero for the relevant vibrational mode.

It is also of interest to consider the particular case of partial resolution of the Rayleigh band into the Rayleigh line and the pure rotational Raman wings which flank it. Again using (1.28) with (1.20c) and tables 1.3a and 1.3b we obtain the averaged Rayleigh CIDs

$$\Delta_x = \frac{2}{c}\Big\{45\alpha G'+\frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK}/kT}}{\sum_{JK}(2J+1)e^{-E_{JK}/kT}}(\alpha_{\|}-\alpha_{\perp})\Big[7(G'_{\|}-G'_{\perp})$$
$$+\omega A_{XYZ}\Big]\Big\}$$

$$\times\left\{45\alpha^2+\frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}}\left[7(\alpha_{\|}-\alpha_{\perp})^2\right]\right\}^{-1} \tag{1.32a}$$

$$\Delta_z = \frac{2\left[(G'_{\|}-G'_{\perp})-\frac{1}{3}\omega A_{XYZ}\right]}{c(\alpha_{\|}-\alpha_{\perp})} \tag{1.32b}$$

and the averaged Raman wing CIDs

$$\Delta_x = \frac{2\left[7(G'_{\|}-G'_{\perp})+\omega A_{XYZ}\right]}{7c(\alpha_{\|}-\alpha_{\perp})} \tag{1.33a}$$

$$\Delta_z = \frac{2\left[(G'_{\|}-G'_{\perp})-\frac{1}{3}\omega A_{XYZ}\right]}{c(\alpha_{\|}-\alpha_{\perp})} \tag{1.33b}$$

The high temperature classical limit of (1.32a) may be obtained by using [17,30]

$$\lim_{T\to\infty}\frac{\sum_{J,K}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{J,K}(2J+1)e^{-E_{JK/kT}}} = \frac{1}{8}\left[\left(2+\frac{21}{\beta}+\frac{27}{\beta^2}\right)-\left(\frac{12}{\beta}+\frac{27}{\beta^2}\right)(1+\beta^2)^{\frac{1}{2}}\frac{\operatorname{arcsinh}\sqrt{\beta}}{\sqrt{\beta}}\right] \tag{1.34}$$

where

$$\beta = \left(\frac{B}{A}-1\right) \tag{1.35}$$

and A, B are the rotational constants of the particular symmetric top molecule.

1.3 Discussion

The rotational transformation properties of a tensor operator are independent of the physical nature of that operator. Thus, the contributions to the numerator and denominator of the dimensionless CIDs, while differentiated by the intrinsic character of their scattering mechanism, are identical in their spatial parts as described by the $D^k_{J'K',JK}$ factors. The polarized component of scattering for totally symmetric modes of vibration with $\Delta J = \Delta K = 0$ is composed of isotropic and anisotropic parts and consequently depends on two $D^k_{J'K',JK}$ factors of ranks zero

and two respectively. In all other cases there is no isotropic scattering and for a given transition, all contributing terms are a function of the same single $D^k_{J'K',JK}$ factor of rank two. In forming the ratio of discriminatory and non-discriminatory parts, these $D^k_{J'K',JK}$ factors cancel. Thus, the dimensionless CIDs, aside from the noted exception, do not depend on the quantum numbers which characterise the rotational states and are independent of temperature.

For non-totally symmetric modes of vibration with exclusively $\Delta K = \pm 1$ or $\Delta K = \pm 2$ and for depolarized scattering in symmetric modes of vibration ($\Delta K = 0$) the CIDs for individual transitions given by (1.26), (1.27) and (1.24b) respectively are identical to those for the set of rovibrational bands associated with that particular vibrational mode. Therefore, no new information about internal molecular parameters is made available by spectral resolution.

For non-totally symmetric modes of vibration with both $\Delta K = \pm 1$ and $\Delta K = \pm 2$ allowed, it may be seen on comparing (1.30) for the unresolved envelope of rovibrational bands to (1.26) and (1.27) for individual transitions that some simpification in analysis arises from resolving bands of different ΔK.

In order to extract maximum information from totally symmetric bands in polarized ROA, it is sufficient that the manifold of unresolved rovibrational bands be resolved from the central purely vibrational line, because the separate rovibrational transitions all show the same CID (1.25a) while that of the parent line (1.24a) is different. The same arguments as those set out for a totally symmetric vibrational band hold for the Rayleigh line and its wings which originate in purely rotational transitions. Pure rotational ROA is of special interest because the CIDs then become simple functions of the polarizability and optical activity property tensor components. It should be possible to deduce the two optical activity anisotropies $(G'_{||} - G'_{\perp})$ and A_{XYZ} from experimentally determined polarized and depolarized CIDs using (1.33) provided that the separation of the Rayleigh line from the rotational Raman envelope is feasible and that a value for the polarizability anisotropy

$(\alpha_{||} - \alpha_{\perp})$ is available. In fact, for small molecules at least, isolation of the Rayleigh line in conventional spectra has been demonstrated to be possible. There are, moreover, various ways of obtaining $(\alpha_{||} - \alpha_{\perp})$. Depolarization ratios yield $|(\alpha_{||} - \alpha_{\perp})|$ and the appropriate sign can often be determined by use of bond polarizability models. The Kerr effect also supplies a value for $(\alpha_{||} - \alpha_{\perp})$ with the advantage of no sign ambiguity [17,37].

If in addition to $(\alpha_{||} - \alpha_{\perp})$ values of α and G' are known from other measurements such as the refractive index for α and optical rotation for G', then in the absence of any resolution, (1.29) for the polarized and depolarized CIDs integrated over the whole Rayleigh band may be used to extract values of $(G'_{||} - G'_{\perp})$ and A_{XYZ}. However, the former method of determining optical activity tensor anisotropies is preferable as it presupposes a knowledge of fewer components of molecular property tensors.

A group polarizability model has been used to calculate the pure Raman optical activity in a chiral conformation (D_3) of triphenylborane [10]. This model involves splitting a molecule into its constituent groups and assigning to each group an intrinsic polarizability and where appropriate intrinsic optical activity tensors defined relative to a local axes system. The global tensor components may then be written as a sum over local tensor components including the origin dependent parts of the optical activity tensors which allow optical activity to be generated from the chiral disposition in space of locally achiral groups [1]. Although the left and right-handed conformers cannot be resolved, this simple example provides a useful basis for more complicated group polarizability calculations of rotational ROA in molecules of lower symmetry. Moreover, the calculated CIDs are large enough to suggest that rotational ROA could be observed using currently available instrumentation.

1.3.1 Symmetry and rotational Raman optical activity

For a dynamic system, if chirality is equated with the ability of that system to display optical activity, then chirality is no longer synonymous with the possession of distinct mirror image forms [38,39]. It is therefore instructive to probe more deeply into the fundamental symmetry aspects of rotational ROA to clarify the concept of chirality in relation to rotating molecules and to discuss the attributes required by a symmetric top for it to be optically active.

The rotational ROA observable has odd parity. There are many other instances of odd-parity observables of which the space-fixed electric dipole is a familiar example. Odd-parity observables are only displayed by systems in mixed parity states, but the exact nature of these mixed parity states depends on the specific observable and requires further analysis.

Consider the space-fixed electric dipole. A typical matrix element for a symmetric top may be written as follows:

$$\begin{aligned} \langle n, JKM \mid \mu_\alpha \mid n, JKM \rangle &= \langle JKM \mid \ell_{\alpha Z} \mid JKM \rangle \overline{\mu}_Z \\ &= \langle JKM \mid P^\dagger (P \ell_{\alpha Z} P^{-1}) P \mid JKM \rangle \overline{\mu}_Z \\ &= -\langle J-KM \mid \ell_{\alpha Z} \mid J-KM \rangle \overline{\mu}_Z \end{aligned} \tag{1.36}$$

where we have introduced the parity operator P. In the final step of (1.36) we have used

$$P|JKM\rangle = \pm|J-KM\rangle \tag{1.37}$$

$$P \ell_{\alpha Z} P^{-1} = \ell_{-\alpha Z} = -\ell_{\alpha Z} \tag{1.38}$$

To justify (1.38) we note that within the passive convention P involves inversion of the space-fixed axes accompanied by inversion of the molecule-fixed axes. However, as the sense of the Z-axis must not vary relative to the nuclei, the change in handedness of the molecule-fixed axes requires a reversal of either the X or Y axes [1].

It is seen that the odd-parity space-fixed operator $\hat{\mu}_\alpha$ is split into the product of an odd-parity direction cosine operator acting on the external rotational state and an even-parity molecule-fixed operator $\hat{\mu}_Z$ acting on the internal vibronic state. Clearly, mixed parity is a required characteristic of the rotational part of the total wavefunction if the matrix element is to be non-zero. Moreover, corresponding matrix elements are equal and opposite for states $|JKM\rangle$ and $|J-KM\rangle$. A parity-odd influence such as an electric field is necessary to lift the degeneracy of these states, thus preventing complete cancellation and allowing some physically observable expression of the matrix element, as seen, for example, in the first-order Stark effect.

We now turn to rotational ROA, for which the symmetry characteristics are best exposed by expressing the associated matrix elements in spherical tensor form, although arguments involving direction cosines analogous to those presented for the space-fixed electric dipole are available. It is clear from the expression for an intensity factor (1.19) that the contributing spherical tensor components of $\hat{\boldsymbol{\alpha}}$, $\hat{\mathbf{G}}$ and $\hat{\mathbf{A}}$ are constrained to be identical for a given transition. This is only possible in a chiral molecule. However, it might be suggested that $|JKM\rangle$ and $|J-KM\rangle$ are enantiomeric and introduce a secondary source of chirality since these states are interconverted by P. To refute this we recall the $D^k_{J'K',JK}$ factor relation (1.20a) which dictates that the intensity factors, and thus CIDs, be invariant to replacement of K by $-K$ and K' by $-K'$, that is, invariant to the parity operation on the rotational states. It is seen that, while the electric dipole observable is composed of an odd-parity spatial part and even-parity internal part, the rotational ROA observable is composed of an even-parity spatial part and odd-parity internal part supported by the mixed parity internal states of the chiral molecule.

To summarize, we note that the unifying feature of all phenomena associated with odd-parity observables is the requirement for distinct mirror image forms. However, it is important to realise that the possession of mirror image forms is

a necessary but not sufficient condition. For example, a chiral asymmetric top does not show a first-order Stark effect, and a rotating achiral symmetric top is not optically active. In the case of optical activity, structural mirror images are necessary, as provided by molecular enantiomers. In the case of the first-order Stark effect it is the dynamic mirror images of symmetric tops rotating in opposite directions relative to the symmetry axis which are needed.

Chapter 2

Raman optical activity in asymmetric top molecules

2.1 Introduction

Until relatively recently, the complexity of the calculation of Raman intensities for rotational transitions in asymmetric tops and the experimental difficulty of obtaining high resolution spectra of gas phase samples dissuaded workers in the field from attempting to perform intensity calculations for asymmetric tops other than those for which an accidentally symmetric top model was a reasonable approximation [40]. Improvements in instrumentation and a replacement of the conventional direction cosine by the irreducible spherical tensor formalism have provided mathematical and technological tools of sufficient sophistication to overcome earlier difficulties.

It would now seem appropriate to undertake a rigorous treatment of rotational ROA in asymmetric tops by extending the theory of rotational ROA in symmetric tops presented in the preceding chapter.

Before deriving completely generalized intensity expressions, a preliminary inves-

tigation of the accidentally symmetric top provides a useful stepping stone between the relatively simple case of the geometric symmetric top and the algebraically more complex case of the asymmetric top.

2.2 Theory

2.2.1 The accidentally symmetric top

The possession of a higher than twofold axis of symmetry by a molecule implies that it has two identical principal moments of inertia, and is thus a symmetric top. However, there may be molecules of lower symmetry for which two of the principal moments of inertia happen to be equal. For such accidentally symmetric tops, the principal axes of the moment of inertia ellipsoid do not necessarily coincide with those of the polarizability ellipsoid. In consequence, the selection rules for rotational and rovibrational Raman scattering in the accidentally symmetric top are different from those given for the geometric symmetric top for which the axes systems are constrained to coincide. The rules now depend on the distribution of non-zero components of polarizability among the irreducible representations of the appropriate asymmetric top point group. However, the inertial properties of the accidentally symmetric top allow us to specify rotational states with the familiar symmetric top quantum numbers J, K and M.

To obtain the dimensionless CIDs for individual rotational and rovibrational transitions in accidentally symmetric tops we recognise that the series of equations (1.24) to (1.27) describing the CIDs for a given ΔK in geometric symmetric tops are merely a particular form of a more general set of equations applicable to all symmetric tops. Removing the specific interrelations of tensor components, ($\alpha_{XX} = \alpha_{YY} = \alpha_{\perp}$, for example) and identifications of vibrational type with ΔK which are characteristic of the geometric symmetric top, we find the following CIDs:

$\Delta J = 0,\ \Delta K = 0$

$$\begin{aligned}\Delta_x &= \frac{2}{c}\left\{45\alpha G' + \frac{[3K^2 - J(J+1)]^2}{J(J+1)(2J+3)(2J-1)}\,[\alpha_{ZZ} - \frac{1}{2}(\alpha_{XX} + \alpha_{YY})]\right. \\ &\quad \left.\times\left[7[G'_{ZZ} - \frac{1}{2}(G'_{XX} + G'_{YY})] + \frac{\omega}{2}(A_{XYZ} - A_{YZX})\right]\right\} \\ &\quad \times\left\{45\alpha^2 + \frac{7[3K^2 - J(J+1)]^2}{J(J+1)(2J+3)(2J-1)}[\alpha_{ZZ} - \frac{1}{2}(\alpha_{XX} + \alpha_{YY})]^2\right\}^{-1} \qquad (2.1a)\end{aligned}$$

$$\Delta_z = \frac{2\left[[G'_{ZZ} - \frac{1}{2}(G'_{XX} + G'_{YY})] - \frac{\omega}{6}(A_{XYZ} - A_{YZX})\right]}{c[\alpha_{ZZ} - \frac{1}{2}(\alpha_{XX} + \alpha_{YY})]} \qquad (2.1b)$$

$\Delta J = \pm 1, \pm 2,\ \Delta K = 0$

$$\Delta_x = \frac{2\left[7[G'_{ZZ} - \frac{1}{2}(G'_{XX} + G'_{YY})] + \frac{\omega}{2}(A_{XYZ} - A_{YZX})\right]}{7c[\alpha_{ZZ} - \frac{1}{2}(\alpha_{XX} + \alpha_{YY})]} \qquad (2.2a)$$

$$\Delta_z = \frac{2\left[[G'_{ZZ} - \frac{1}{2}(G'_{XX} + G'_{YY})] - \frac{\omega}{6}(A_{XYZ} - A_{YZX})\right]}{c[\alpha_{ZZ} - \frac{1}{2}(\alpha_{XX} + \alpha_{YY})]} \qquad (2.2b)$$

$\Delta J = 0, \pm 1, \pm 2,\ \Delta K \pm 1$

$$\begin{aligned}\Delta_x &= \frac{1}{c}\left[\alpha_{XZ}(G'_{XZ} + G'_{ZX}) + \alpha_{YZ}(G'_{YZ} + G'_{ZY})\right. \\ &\quad + \frac{\omega}{21}[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX}) \\ &\quad \left. - \alpha_{XZ}(A_{ZZY} - A_{YZZ} + A_{YXX} - A_{XXY})]\right] \\ &\quad \times(\alpha_{XZ}^2 + \alpha_{YZ}^2)^{-1} \qquad (2.3a)\end{aligned}$$

$$\begin{aligned}\Delta_z &= \frac{1}{c}\left[\alpha_{XZ}(G'_{XZ} + G'_{ZX}) + \alpha_{YZ}(G'_{YZ} + G'_{ZY})\right. \\ &\quad - \frac{\omega}{9}[\alpha_{YZ}(A_{ZZX} - A_{XZZ} + A_{XYY} - A_{YYX}) \\ &\quad \left. - \alpha_{XZ}(A_{ZZY} - A_{YZZ} + A_{YXX} - A_{XXY})]\right] \\ &\quad \times(\alpha_{XZ}^2 + \alpha_{YZ}^2)^{-1} \qquad (2.3b)\end{aligned}$$

$\Delta J = 0, \pm 1, \pm 2,\ \Delta K = \pm 2$

$$\begin{aligned}\Delta_x &= \frac{2}{c}\left[(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY}) + 2\alpha_{XY}(G'_{XY} + G'_{YX})\right. \\ &\quad - \frac{\omega}{21}[(\alpha_{XX} - \alpha_{YY})(2A_{ZXY} - A_{XYZ} - A_{YZX}) \\ &\quad \left. + 2\alpha_{XY}(A_{XXZ} - A_{ZXX} + A_{ZYY} - A_{YYZ})]\right] \\ &\quad \times[(\alpha_{XX} - \alpha_{YY})^2 + 4\alpha_{XY}^2]^{-1} \qquad (2.4a)\end{aligned}$$

$$\begin{aligned}\Delta_z &= \frac{2}{c}\Big[(\alpha_{XX}-\alpha_{YY})(G'_{XX}-G'_{YY})+2\alpha_{XY}(G'_{XY}+G'_{YX})\\ &\quad +\frac{\omega}{9}\Big[(\alpha_{XX}-\alpha_{YY})(2A_{ZXY}-A_{XYZ}-A_{YZX})\\ &\quad +2\alpha_{XY}(A_{XXZ}-A_{ZXX}+A_{ZYY}-A_{YYZ})\Big]\Big]\\ &\quad \times[(\alpha_{XX}-\alpha_{YY})^2+4\alpha_{XY}^2]^{-1} \qquad (2.4b)\end{aligned}$$

The unresolved CIDs for a vibrational band may be obtained by summing over all allowed final states and then averaging over the initial states as detailed in chapter one. For example, the unresolved CIDs for a totally symmetric mode of vibration in an accidentally symmetric top of C_1 symmetry are

$$\begin{aligned}\Delta_x &= \frac{2}{c}\Big[45\alpha G'+\frac{7}{2}\Big[(\alpha_{ZZ}-\alpha_{XX})(G'_{ZZ}-G'_{XX})\\ &\quad +(\alpha_{ZZ}-\alpha_{YY})(G'_{ZZ}-G'_{YY})+(\alpha_{XX}-\alpha_{YY})(G'_{XX}-G'_{YY})\\ &\quad +3[\alpha_{XZ}(G'_{XZ}+G'_{ZX})+\alpha_{YZ}(G'_{YZ}+G'_{ZY})+\alpha_{XY}(G'_{XY}+G'_{YX})]\Big]\\ &\quad +\frac{\omega}{2}[(\alpha_{XX}-\alpha_{ZZ})A_{YZX}+(\alpha_{YY}-\alpha_{XX})A_{ZXY}+(\alpha_{ZZ}-\alpha_{YY})A_{XZY}\\ &\quad +\alpha_{XZ}(A_{XXY}-A_{YXX}+A_{YZZ}-A_{ZZY})\\ &\quad +\alpha_{YZ}(A_{XYY}-A_{YYX}+A_{ZZX}-A_{XZZ})\\ &\quad +\alpha_{XY}(A_{ZXX}-A_{XXZ}+A_{YYZ}-A_{ZYY})]\Big]\\ &\quad \times\Big[45\alpha^2+\frac{7}{2}[(\alpha_{ZZ}-\alpha_{XX})^2+(\alpha_{ZZ}-\alpha_{YY})^2+(\alpha_{XX}-\alpha_{YY})^2\\ &\quad +6(\alpha_{XZ}^2+\alpha_{YZ}^2+\alpha_{XY}^2)]\Big]^{-1} \qquad (2.5a)\end{aligned}$$

$$\begin{aligned}\Delta_z &= \frac{2}{c}\Big[(\alpha_{ZZ}-\alpha_{XX})(G'_{ZZ}-G'_{XX})+(\alpha_{ZZ}-\alpha_{YY})(G'_{ZZ}-G'_{YY})\\ &\quad +(\alpha_{XX}-\alpha_{YY})(G'_{XX}-G'_{YY})\\ &\quad +3\left[\alpha_{XZ}(G'_{XZ}+G'_{ZX})+\alpha_{YZ}(G'_{YZ}+G'_{ZY})+\alpha_{XY}(G'_{XY}+G'_{YX})\right]\\ &\quad -\frac{\omega}{3}\left[(\alpha_{XX}-\alpha_{ZZ})A_{YZX}+(\alpha_{YY}-\alpha_{XX})A_{ZXY}\right.\\ &\quad \left.+(\alpha_{ZZ}-\alpha_{YY})A_{XZY}\right.\\ &\quad +\alpha_{XZ}(A_{XXY}-A_{YXX}+A_{YZZ}-A_{ZZY})\\ &\quad +\alpha_{YZ}(A_{XYY}-A_{YYX}+A_{ZZX}-A_{XZZ})\end{aligned}$$

$$+\alpha_{XY}(A_{ZXX} - A_{XXZ} + A_{YYZ} - A_{ZYY})]\Big]$$
$$\times[(\alpha_{ZZ} - \alpha_{XX})^2 + (\alpha_{ZZ} - \alpha_{YY})^2 + (\alpha_{XX} - \alpha_{YY})^2$$
$$+6(\alpha_{XZ}^2 + \alpha_{YZ}^2 + \alpha_{XY}^2)]^{-1} \tag{2.5b}$$

These results are consistent with (1.31) for Rayleigh scattering from an isotropic fluid of molecules of C_1 symmetry. Comparing (1.29) to (2.5) reveals the extent to which expressions for the unresolved CIDs are complicated by introducing an inequivalence of principal inertial and principal polarizability axes. However, simplification of the form of (2.5) is possible.

We may rewrite (2.5) as [1]

$$\Delta_x = \frac{2[45\alpha G' + 7\beta(G')^2 + \beta(A)^2]}{c[45\alpha^2 + 7\beta(\alpha)^2]} \tag{2.6a}$$
$$\Delta_z = \frac{2[\beta(G')^2 - \frac{1}{3}\beta(A)^2]}{c\beta(\alpha)^2} \tag{2.6b}$$

where we have introduced the following frame-independent combinations:

$$\begin{aligned}
\beta(\alpha)^2 &= \frac{1}{2}(3\alpha_{\alpha\beta}\alpha_{\alpha\beta} - \alpha_{\alpha\alpha}\alpha_{\beta\beta}) \\
&= \frac{1}{2}[(\alpha_{XX} - \alpha_{YY})^2 + (\alpha_{XX} - \alpha_{ZZ})^2 + (\alpha_{YY} - \alpha_{ZZ})^2 \\
&\quad +6(\alpha_{XY}^2 + \alpha_{XZ}^2 + \alpha_{YZ}^2)] \qquad (2.7) \\
\beta(G')^2 &= \frac{1}{2}(3\alpha_{\alpha\beta}G'_{\alpha\beta} - \alpha_{\alpha\alpha}G'_{\beta\beta}) \\
&= \frac{1}{2}\Big[(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY}) + (\alpha_{XX} - \alpha_{ZZ})(G'_{XX} - G'_{ZZ}) \\
&\quad +(\alpha_{YY} - \alpha_{ZZ})(G'_{YY} - G'_{ZZ}) + 3[\alpha_{XY}(G'_{XY} + G'_{YX}) \\
&\quad +\alpha_{XZ}(G'_{XZ} + G'_{ZX}) + \alpha_{YZ}(G'_{YZ} + G'_{ZY})]\Big] \qquad (2.8) \\
\beta(A)^2 &= \frac{1}{2}\omega\alpha_{\alpha\beta}\epsilon_{\alpha\gamma\delta}A_{\gamma\delta\beta} \\
&= \frac{1}{2}\omega[(\alpha_{YY} - \alpha_{XX})A_{ZXY} + (\alpha_{XX} - \alpha_{ZZ})A_{YZX} + (\alpha_{ZZ} - \alpha_{YY})A_{XZY} \\
&\quad +\alpha_{XY}(A_{ZXX} - A_{XXZ} + A_{YYZ} - A_{ZYY}) \\
&\quad +\alpha_{XZ}(A_{XXY} - A_{YXX} + A_{YZZ} - A_{ZZY}) \\
&\quad +\alpha_{YZ}(A_{XYY} - A_{YYX} + A_{ZZX} - A_{XZZ})] \qquad (2.9)
\end{aligned}$$

It is useful to note that (2.5), being exclusively functions of tensor invariants α, G', $\beta(\alpha)^2$, $\beta(G')^2$ and $\beta(A)^2$ may be immediately rewritten in canonical form by taking tensorial components relative to the principal axes of polarizability rather than the principal axes of inertia.

It is also possible to derive equations analogous to (1.32) and (1.33) which give the CIDs applicable in the case of resolution of the pure rotational Raman wings from the central Rayleigh line. The CIDs for the Rayleigh line averaged over all initial rotational states for a molecule of C_1 symmetry are

$$\begin{aligned}\Delta_x &= \frac{2}{c}\Bigg\{45\alpha G' + \frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}} \\ &\quad \times[2\alpha_{ZZ} - (\alpha_{XX}+\alpha_{YY})] \\ &\quad \times\left[\frac{7}{4}[2G'_{ZZ} - (G'_{XX}+G'_{YY})] + \frac{\omega}{4}(A_{XYZ} - A_{YXZ})\right] \\ &\quad \times\Bigg\{45\alpha^2 + \frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}} \\ &\quad \times\frac{7}{4}[2\alpha_{ZZ} - (\alpha_{XX}+\alpha_{YY})]^2\Bigg\}^{-1} \qquad (2.10a)\end{aligned}$$

$$\Delta_z = \frac{2[2G'_{ZZ} - (G'_{XX}+G'_{YY}) - \frac{1}{3}\omega(A_{XYZ} - A_{YZX})]}{c[2\alpha_{ZZ} - (\alpha_{XX}+\alpha_{YY})]} \qquad (2.10b)$$

The corresponding CIDs for the combined Stokes and anti-Stokes rotational Raman wings are

$$\begin{aligned}\Delta_x &= \frac{2}{c}\Big[[2\alpha_{ZZ} - (\alpha_{XX}+\alpha_{YY})]\Big[7[2G'_{ZZ} - (G'_{XX}+G'_{YY})] \\ &\quad +\omega(A_{XYZ} - A_{YXZ})\Big] \\ &\quad \times\left[1 - \frac{\sum_{J,K}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}}\right] \\ &\quad +42[\alpha_{XZ}(G'_{XZ}+G'_{ZX}) + \alpha_{YZ}(G'_{YZ}+G'_{ZY}) + \alpha_{XY}(G'_{XY}+G'_{YX}) \\ &\quad +\frac{1}{2}(\alpha_{XX} - \alpha_{YY})(G'_{XX} - G'_{YY})] \\ &\quad +\omega[2\alpha_{XZ}(A_{XXY} - A_{YXX} + A_{YZZ} - A_{ZZY}) \\ &\quad +2\alpha_{YZ}(A_{XYY} - A_{YYX} + A_{ZZX} - A_{XZZ}) \\ &\quad +2\alpha_{XY}(A_{ZXX} - A_{XXZ} + A_{YYZ} - A_{ZYY}) \\ &\quad +(\alpha_{YY} - \alpha_{XX})(2A_{ZXY} - A_{XYZ} - A_{YZX})]\Big]\end{aligned}$$

$$\times\left[7[2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY})]^2\left[1-\frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}}\right]\right.$$
$$\left.+84[(\alpha^2_{XZ}+\alpha^2_{YZ}+\alpha^2_{XY})+\frac{1}{4}(\alpha_{XX}-\alpha_{YY})^2]\right]^{-1} \qquad (2.11a)$$

$$\begin{aligned}\Delta_z &= \frac{2}{c}\left[[2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY})][2G'_{ZZ}-(G'_{XX}+G'_{YY})]\right.\\
&\left.-\frac{\omega}{3}(A_{XYZ}-A_{YXZ})\right]\\
&\times\left[1-\frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}}\right]\\
&+3[2\alpha_{XZ}(G'_{XZ}+G'_{ZX})+2\alpha_{YZ}(G'_{YZ}+G'_{ZY})+2\alpha_{XY}(G'_{YX}+G'_{XY})\\
&+(\alpha_{XX}-\alpha_{YY})(G'_{XX}-G'_{YY})]\\
&-\frac{\omega}{3}[2\alpha_{XZ}(A_{XXY}-A_{YXX}+A_{YZZ}-A_{ZZY})\\
&+2\alpha_{YZ}(A_{XYY}-A_{YYX}+A_{ZZX}-A_{XZZ})\\
&+2\alpha_{XY}(A_{ZXX}-A_{XXZ}+A_{YYZ}-A_{ZYY})\\
&+(\alpha_{YY}-\alpha_{XX})(2A_{ZXY}-A_{XYZ}-A_{YZX})]\Bigg]\\
&\times\left[[2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY})]^2\left[1-\frac{\sum_{JK}(2J+1)D^2_{JK,JK}e^{-E_{JK/kT}}}{\sum_{JK}(2J+1)e^{-E_{JK/kT}}}\right]\right.\\
&\left.+12[(\alpha^2_{XZ}+\alpha^2_{YZ}+\alpha^2_{XY})+\frac{1}{4}(\alpha_{XX}-\alpha_{YY})^2]\right]^{-1} \qquad (2.11b)\end{aligned}$$

We shall not write down explicitly the results equivalent to (2.5) to (2.11) for all possible asymmetric top point groups. For asymmetric tops of higher symmetry, it is obvious that these equations require modification consistent with the transformation properties of the relevant polarizability and optical activity components as given by the character tables of group theory.

The high temperature classical limit of (2.10a) and (2.11) for a specific molecule may be obtained by using (1.34).

2.2.2 Intensity factors

In chapter one, we defined intensity factors (1.15) for rovibrational transitions in symmetric tops. In an analogous way, we define intensity factors for rovibrational transitions $n', J'\mathcal{T}'M' \leftarrow n, J\mathcal{T}M$ in asymmetric tops. The $\mathcal{T}$ label is an integer $-J \leq \mathcal{T} \leq J$ which is assigned such that the lowest energy level of a J manifold has $\mathcal{T} = -J$ and the value of $\mathcal{T}$ increases with increasing energy up to the highest energy level with $\mathcal{T} = J$. An alternative labelling scheme associates the limiting case prolate and oblate top K quantum numbers to each level. Thus, for a transition $n', J'\mathcal{T}'M' \leftarrow n, J\mathcal{T}M$ we define an intensity factor corresponding to a $\hat{\mathbf{T}}\hat{\mathbf{S}}$ scattering contribution:

$$[I_q^k(TS)]_{n'J'\mathcal{T}',nJ\mathcal{T}} = \frac{1}{(2J+1)} \sum_{MM'} \langle n', J'\mathcal{T}'M' \mid \hat{T}_q^k \mid n, J\mathcal{T}M \rangle \times \langle n', J'\mathcal{T}'M' \mid \hat{S}_q^k \mid n, J\mathcal{T}M \rangle^* \tag{2.12}$$

It is possible to write $|n, J\mathcal{T}M\rangle$ as a linear combination of Wang functions

$$|n, J\mathcal{T}M\rangle = \sum_K a_K^{J\mathcal{T}} |n, JKM\gamma\rangle \tag{2.13}$$

The summation is over K exclusively even or odd, and the Wang functions are definite parity symmetric or antisymmetric combinations of symmetric top functions:

$$|n, JKM\gamma\rangle = \frac{1}{\sqrt{2}} \left[|n, JKM\rangle + (-1)^\gamma |n, J-KM\rangle \right], K > 0 \tag{2.14}$$

where γ is exclusively even or odd for a given summation. The rotational energy Hamiltonian for an asymmetric top may be set up in the Wang function basis and diagonalized using standard methods to obtain the eigenvalues and eigenfunctions. These can be classified according to their symmetry by E^+, E^-, O^+, O^- where E or O denote whether even or odd values of K are involved in the summation (2.13), and $+$ or $-$ indicate the even or oddness of γ [32,41,42].

The asymmetric top matrix elements in (2.12) may be expressed as a combination of symmetric top matrix elements by using (2.13) and (2.14). It is then possible

to apply the Wigner-Eckart theorem for axially symmetric systems (1.16) to obtain [40]

$$
\begin{aligned}
\langle n', J'T'M' \mid \hat{T}^k_q \mid n, JTM \rangle \;=\; & i^{J+J'}(-1)^{J'-M'}[(2J+1)(2J'+1)]^{\frac{1}{2}} \\
& \times \begin{pmatrix} J' & k & J \\ -M' & q & M \end{pmatrix} \left\{ \frac{1}{2} \sum_{K=0}^{J} a_K^{J'T'} a_K^{JT} \right. \\
& \times (-1)^K \left[1 + (-1)^{J+J'+k} (-1)^{\gamma+\gamma'} \right] \\
& \times \bar{T}^k_0 \begin{pmatrix} J' & k & J \\ -K & 0 & K \end{pmatrix} + \sum_{K=1}^{J} \sum_{K'=1}^{J'} \sum_{q'=1}^{k} \left[i^{-q'} \bar{T}^k_{q'} \right. \\
& + (-1)^{\gamma+\gamma'} (-1)^{J+J'+k} i^{q'} \bar{T}^k_{-q'} \Big] \\
& \times \left[\frac{(-1)^{K+\gamma}}{\sqrt{2}} a_o^{J'T'} a_K^{JT} \begin{pmatrix} J' & k & J \\ 0 & q' & -K \end{pmatrix} \right. \\
& + \frac{1}{\sqrt{2}} a_{K'}^{J'T'} a_o^{JT} \begin{pmatrix} J' & k & J \\ -K' & q' & 0 \end{pmatrix} \\
& + \frac{(-1)^K}{2} a_{K'}^{J'T'} a_K^{JT} \left[\begin{pmatrix} J' & k & J \\ -K' & q' & K \end{pmatrix} \right. \\
& + (-1)^{\gamma} \begin{pmatrix} J' & k & J \\ -K' & q' & -K \end{pmatrix} \\
& \left. \left. \left. + (-1)^{\gamma+\gamma'} \begin{pmatrix} J' & k & J \\ K' & q' & -K \end{pmatrix} \right] \right] \right\} \qquad (2.15)
\end{aligned}
$$

Inserting (2.15) into (2.12) yields

$$
\begin{aligned}
[I^k_q(TS)]_{n'J'T',nJT} \;=\; & \frac{(2J'+1)}{(2k+1)} \\
& \times \left\{ \frac{1}{2} \sum_{K=0}^{J} a_K^{J'T'} a_K^{JT} (-1)^K \left[1 + (-1)^{J+J'+k} (-1)^{\gamma+\gamma'} \right] \right. \\
& \times \bar{T}^k_0 \begin{pmatrix} J' & k & J \\ -K & 0 & K \end{pmatrix} \\
& \left. + \sum_{K=1}^{J} \sum_{K'=1}^{J'} \sum_{q'=1}^{k} \left[i^{-q'} \bar{T}^k_{q'} + (-1)^{\gamma+\gamma'} (-1)^{J+J'+k} i^{q'} \bar{T}^k_{-q'} \right] \right.
\end{aligned}
$$

$$
\times\left[\frac{(-1)^{K+\gamma}}{\sqrt{2}}a_o^{J'T'}a_K^{JT}\begin{pmatrix} J' & k & J \\ 0 & q' & -K \end{pmatrix}\right.
$$

$$
+\frac{1}{\sqrt{2}}a_{K'}^{J'T'}a_o^{JT}\begin{pmatrix} J' & k & J \\ -K' & q' & 0 \end{pmatrix}
$$

$$
+\frac{(-1)^{K}}{2}a_{K'}^{J'T'}a_K^{JT}\left[\begin{pmatrix} J' & k & J \\ -K' & q' & K \end{pmatrix}\right.
$$

$$
+(-1)^{\gamma}\begin{pmatrix} J' & k & J \\ -K' & q' & -K \end{pmatrix}
$$

$$
\left.\left.+(-1)^{\gamma+\gamma'}\begin{pmatrix} J' & k & J \\ K' & q' & -K \end{pmatrix}\right]\right]\Bigg\}
$$

$$
\times\left\{\frac{1}{2}\sum_{K=0}^{J}a_K^{J'T'}a_K^{JT}(-1)^{K}\left[1+(-1)^{J+J'+k}(-1)^{\gamma+\gamma'}\right]\right.
$$

$$
\times\bar{S}_0^{k*}\begin{pmatrix} J' & k & J \\ -K & 0 & K \end{pmatrix}
$$

$$
\left.+\sum_{K=1}^{J}\sum_{K'=1}^{J'}\sum_{q'=1}^{k}\left[i^{q'}\bar{S}_{q'}^{k*}+(-1)^{\gamma+\gamma'}(-1)^{J+J'+k}i^{-q'}\bar{S}_{-q'}^{k*}\right]\right.
$$

$$
\times\left[\frac{(-1)^{K+\gamma}}{\sqrt{2}}a_o^{J'T'}a_K^{JT}\begin{pmatrix} J' & k & J \\ 0 & q' & -K \end{pmatrix}\right.
$$

$$
+\frac{1}{\sqrt{2}}a_{K'}^{J'T'}a_o^{JT}\begin{pmatrix} J' & k & J \\ -K' & q' & 0 \end{pmatrix}
$$

$$
+\frac{(-1)^{K}}{2}a_{K'}^{J'T'}a_K^{JT}\left[\begin{pmatrix} J' & k & J \\ -K' & q' & K \end{pmatrix}\right.
$$

$$
+(-1)^{\gamma}\begin{pmatrix} J' & k & J \\ -K' & q' & -K \end{pmatrix}
$$

$$
\left.\left.+(-1)^{\gamma+\gamma'}\begin{pmatrix} J' & k & J \\ K' & q' & -K \end{pmatrix}\right]\right]\Bigg\} \tag{2.16}
$$

Rotational selection rules for rotation-vibration Raman scattering depend on the

conditions required for the $3-j$ symbols in (2.16) to be non-zero. In the case of isotropic scattering ($k=0$) these are $\Delta J = \Delta K = 0$, while for anisotropic scattering (k=2) we have $\Delta J = \Delta K = 0, \pm 1, \pm 2$. As for the symmetric top, there are further restrictions on ΔK dependent on whether or not the associated tensor component contributes for a given combination of initial and final vibrational states.

In addition to the aforementioned rules, which are of the same character as those rules given earlier for the symmetric top, there are rotational selection rules which are unique to the asymmetric top. These rules, also obtainable from (2.16), specify the allowed associations of ΔJ with initial and final rotational state symmetry combinations for a given polarizability or optical activity tensor component and are deduced from a consideration of non-vanishing $3-j$ symbols and the combinations of even and odd-valued J, J', γ and γ' required for a specific tensor component to appear in (2.16). The selection rules so derived are listed in table 2.1, which is consistent with Stoicheff [36]. For simplicity we have written the results for a molecule of C_1 symmetry. For other asymmetric top point groups, the relation between components and rotational selection rules are as given and the vibrational species should be obtained from group theoretical considerations.

2.2.3 Vibration-rotation Raman optical activity

In a fashion similar to that detailed for the symmetric top, it is possible to calculate the polarized and depolarized dimensionless CIDs Δ_x and Δ_z associated with allowed rovibrational transitions by correlating an intensity factor $[I_q^k(TS)]_{n'J'T',nJT}$ with each term $\hat{T}_q^k \hat{S}_q^{k*}$ appearing in (1.2) as specified by (1.23). We now list the CIDs for all possible combinations of initial and final state symmetries:

Table 2.1

Selection rules for rovibrational Raman transitions in a chiral asymmetric top of C_1 symmetry.

Vibrational species	Non-zero components of polarizability and optical activity tensors		Selection rules
	Cartesian components	Spherical components	
totally symmetric	$\alpha_{XX}+\alpha_{YY}+\alpha_{ZZ}$	α_0^0	$\Delta J=\Delta\mathcal{T}=0$
	$G'_{XX}+G'_{YY}+G'_{ZZ}$	G'^0_0	
	$2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY}),\alpha_{XX}-\alpha_{YY}$	$\alpha_0^2,\alpha_2^2+\alpha_{-2}^2$	$\Delta J=0,\pm2;E^\pm\rightarrow E^\pm,O^\pm\rightarrow O^\pm$
	$2G'_{ZZ}-(G'_{XX}+G'_{YY}),G'_{XX}-G'_{YY}$	$G'^2_0,G'^2_2+G'^2_{-2}$	$\Delta J=\pm1;E^+\leftrightarrow E^-,O^+\leftrightarrow O^-$
	$A_{XYZ}-A_{YZX},2A_{ZXY}-A_{XYZ}-A_{YZX}$	$A_0^2,A_2^2+A_{-2}^2$	
	α_{XY}	$\alpha_2^2-\alpha_{-2}^2$	$\Delta J=0,\pm2;E^+\leftrightarrow E^-,O^+\leftrightarrow O^-$
	$G'_{XY}+G'_{YX}$	$G'^2_2-G'^2_{-2}$	$\Delta J=\pm1;E^\pm\rightarrow E^\pm,O^\pm\rightarrow O^\pm$
	$A_{XXZ}-A_{ZXX}+A_{ZYY}-A_{YYZ}$	$A_2^2-A_{-2}^2$	
	α_{YZ}	$\alpha_1^2+\alpha_{-1}^2$	$\Delta J=0,\pm2;E^\pm\leftrightarrow O^\mp$
	$G'_{YZ}+G'_{ZY}$	$G'^2_1+G'^2_{-1}$	$\Delta J=\pm1;E^\pm\leftrightarrow O^\pm$
	$A_{XXY}-A_{YYX}+A_{ZZX}-A_{XZZ}$	$A_1^2+A_{-1}^2$	
	α_{XZ}	$\alpha_1^2-\alpha_{-1}^2$	$\Delta J=0,\pm2;E^\pm\leftrightarrow O^\pm$
	$G'_{XZ}+G'_{ZX}$	$G'^2_1-G'^2_{-1}$	$\Delta J=\pm1;E^\pm\leftrightarrow O^\mp$
	$A_{YXX}-A_{XXY}+A_{ZZY}-A_{YZZ}$	$A_1^2-A_{-1}^2$	

$\Delta J = 0, \pm 2;\ E^{\pm} \rightarrow E^{\pm}, O^{\pm} \rightarrow O^{\pm}$

$\Delta J = \pm 1\ ;\ E^{+} \leftrightarrow E^{-}, O^{+} \leftrightarrow O^{-}$

$$
\begin{aligned}
\Delta_x \;=\; & \frac{2}{c}\Bigg\{ 3\alpha G' \delta_{JJ'}\delta_{TT'} + \frac{(2J'+1)}{5}\Bigg[\frac{1}{\sqrt{6}}[2\alpha_{ZZ} - (\alpha_{XX} + \alpha_{YY})] \\
& \times \sum_{K=0}^{J} a_K^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ -K & 0 & K \end{pmatrix} - (\alpha_{XX} - \alpha_{YY}) \sum_{K=1}^{J} \Bigg[\frac{(-1)^{\gamma}}{\sqrt{2}} \\
& \times a_o^{J'T'} a_2^{JT} \begin{pmatrix} J' & 2 & J \\ 0 & 2 & -2 \end{pmatrix} + \frac{(-1)^{K}}{\sqrt{2}} a_2^{J'T'} a_o^{JT} \begin{pmatrix} J' & 2 & J \\ -2 & 2 & 0 \end{pmatrix} \\
& + \frac{1}{2} a_{K+2}^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ -K-2 & 2 & K \end{pmatrix} + \frac{(-1)^{\gamma}}{2} a_{2-K}^{J'T'} a_K^{JT} \\
& \times \begin{pmatrix} J' & 2 & J \\ K-2 & 2 & -K \end{pmatrix} + \frac{(-1)^{\gamma+\gamma'}}{2} a_{K-2}^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ K-2 & 2 & -K \end{pmatrix} \Bigg] \Bigg] \\
& \times \Bigg[\frac{1}{2\sqrt{6}} \Big[7[2G'_{ZZ} - (G'_{XX} + G'_{YY})] + \omega(A_{XYZ} - A_{YZX}) \Big] \\
& \times \sum_{K=0}^{J} a_K^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ -K & 0 & K \end{pmatrix} \\
& - \Big[\frac{7}{2}(G'_{XX} - G'_{YY}) - \frac{\omega}{6}(2A_{ZXY} - A_{XYZ} - A_{YZX}) \Big] \\
& \times \Bigg[\sum_{K=1}^{J} \frac{(-1)^{\gamma}}{\sqrt{2}} a_o^{J'T'} a_2^{JT} \begin{pmatrix} J' & 2 & J \\ 0 & 2 & -2 \end{pmatrix} \\
& + \frac{(-1)^{K}}{\sqrt{2}} a_2^{J'T'} a_o^{JT} \begin{pmatrix} J' & 2 & J \\ -2 & 2 & 0 \end{pmatrix} + \frac{1}{2} a_{K+2}^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ -K-2 & 2 & K \end{pmatrix} \\
& + \frac{(-1)^{\gamma}}{2} a_{2-K}^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ K-2 & 2 & -K \end{pmatrix} \\
& + \frac{(-1)^{\gamma+\gamma'}}{2} a_{K-2}^{J'T'} a_K^{JT} \begin{pmatrix} J' & 2 & J \\ K-2 & 2 & -K \end{pmatrix} \Bigg] \Bigg] \Bigg\}
\end{aligned}
$$

$$\times\Bigg\{3\alpha^2\delta_{JJ'}\delta_{TT'}+\frac{7(2J'+1)}{10}$$

$$\times\Bigg[\frac{1}{\sqrt{6}}[2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY})]\sum_{K=0}^{J}a_K^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ -K & 0 & K\end{pmatrix}$$

$$-(\alpha_{XX}-\alpha_{YY})\sum_{K=1}^{J}\Bigg[\frac{(-1)^\gamma}{\sqrt{2}}a_o^{J'T'}a_2^{JT}\begin{pmatrix}J' & 2 & J\\ 0 & 2 & -2\end{pmatrix}$$

$$+\frac{(-1)^K}{\sqrt{2}}a_2^{J'T'}a_o^{JT}\begin{pmatrix}J' & 2 & J\\ -2 & 2 & 0\end{pmatrix}+\frac{1}{2}a_{K+2}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ -K-2 & 2 & K\end{pmatrix}$$

$$+\frac{(-1)^\gamma}{2}a_{2-K}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ K-2 & 2 & -K\end{pmatrix}$$

$$+(-1)^{\gamma+\gamma'}a_{K-2}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ K-2 & 2 & -K\end{pmatrix}\Bigg]\Bigg]^2\Bigg\}^{-1} \tag{2.17a}$$

$$\Delta_z = \frac{2}{c}\Bigg\{\frac{1}{\sqrt{6}}\Big[[2G'_{ZZ}-(G'_{XX}+G'_{YY})]-\frac{\omega}{3}(A_{XYZ}-A_{YZX})\Big]$$

$$\times\sum_{K=0}^{J}a_K^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ -K & 0 & K\end{pmatrix}-[(G'_{XX}-G'_{YY})$$

$$+\frac{\omega}{9}(2A_{ZXY}-A_{XYZ}-A_{YZX})]\sum_{K=1}^{J}\Bigg[\frac{(-1)^\gamma}{\sqrt{2}}a_o^{J'T'}a_2^{JT}\begin{pmatrix}J' & 2 & J\\ 0 & 2 & -2\end{pmatrix}$$

$$+\frac{(-1)^K}{\sqrt{2}}a_2^{J'T'}a_o^{JT}\begin{pmatrix}J' & 2 & J\\ -2 & 2 & 0\end{pmatrix}+\frac{1}{2}a_{K+2}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ -K-2 & 2 & K\end{pmatrix}$$

$$+\frac{(-1)^\gamma}{2}a_{2-K}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ K-2 & 2 & -K\end{pmatrix}$$

$$+\frac{(-1)^{\gamma+\gamma'}}{2}a_{K-2}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ K-2 & 2 & -K\end{pmatrix}\Bigg]\Bigg\}$$

$$\times\Bigg\{\frac{1}{\sqrt{6}}[2\alpha_{ZZ}-(\alpha_{XX}+\alpha_{YY})]\sum_{K=0}^{J}a_{K'}^{J'T'}a_K^{JT}\begin{pmatrix}J' & 2 & J\\ -K & 0 & K\end{pmatrix}$$

$$-(\alpha_{XX}-\alpha_{YY})\sum_{K=1}^{J}\left[\frac{(-1)^{\gamma}}{\sqrt{2}}a_{o}^{J'T'}a_{2}^{JT}\begin{pmatrix} J' & 2 & J \\ 0 & 2 & -2 \end{pmatrix}\right.$$

$$+\frac{(-1)^{K}}{\sqrt{2}}a_{2}^{J'T'}a_{o}^{JT}\begin{pmatrix} J' & 2 & J \\ -2 & 2 & 0 \end{pmatrix}+\frac{1}{2}a_{K+2}^{J'T'}a_{K}^{JT}\begin{pmatrix} J' & 2 & J \\ -K-2 & 2 & K \end{pmatrix}$$

$$+\frac{(-1)^{\gamma}}{2}a_{2-K}^{J'T'}a_{K}^{JT}\begin{pmatrix} J' & 2 & J \\ K-2 & 2 & -K \end{pmatrix}$$

$$\left.+\frac{(-1)^{\gamma+\gamma'}}{2}a_{K-2}^{J'T'}a_{K}^{JT}\begin{pmatrix} J' & 2 & J \\ K-2 & 2 & -K \end{pmatrix}\right]\Bigg\}^{-1} \tag{2.17b}$$

$\Delta J = 0, \pm 2;\ E^{+} \leftrightarrow E^{-},\ O^{+} \leftrightarrow O^{-}$

$\Delta J = \pm 1;\ E^{\pm} \rightarrow E^{\pm},\ O^{\pm} \rightarrow O^{\pm}$

$$\Delta_x = \frac{[(G'_{XY}+G'_{YX})-\frac{1}{21}\omega(A_{XXZ}-A_{ZXX}+A_{ZYY}-A_{YYZ})]}{c\alpha_{XY}} \tag{2.18a}$$

$$\Delta_z = \frac{[(G'_{XY}+G'_{YX})+\frac{1}{9}\omega(A_{XXZ}-A_{ZXX}+A_{ZYY}-A_{YYZ})]}{c\alpha_{XY}} \tag{2.18b}$$

$\Delta J = 0, \pm 2;\ E^{\pm} \leftrightarrow O^{\mp}$

$\Delta J = \pm 1;\ E^{\pm} \leftrightarrow O^{\pm}$

$$\Delta_x = \frac{[(G'_{YZ}+G'_{ZY})+\frac{1}{21}\omega(A_{XYY}-A_{YYX}+A_{ZZX}-A_{XZZ})]}{c\alpha_{YZ}} \tag{2.19a}$$

$$\Delta_z = \frac{[(G'_{YZ}+G'_{ZY})-\frac{1}{9}\omega(A_{XYY}-A_{YYX}+A_{ZZX}-A_{XZZ})]}{c\alpha_{YZ}} \tag{2.19b}$$

$\Delta J = 0, \pm 2;\ E^{\pm} \leftrightarrow O^{\pm}$

$\Delta J = \pm 1;\ E^{\pm} \leftrightarrow O^{\mp}$

$$\Delta_x = \frac{[(G'_{XZ}+G'_{ZX})-\frac{1}{21}\omega(A_{YXX}-A_{XXY}+A_{ZZY}-A_{YZZ})]}{c\alpha_{XZ}} \tag{2.20a}$$

$$\Delta_z = \frac{[(G'_{XZ}+G'_{ZX})+\frac{1}{9}\omega(A_{YXX}-A_{XXY}+A_{ZZY}-A_{YZZ})]}{c\alpha_{XZ}} \tag{2.20b}$$

2.2.4 Intensity sum rules

For both the inertial and geometric symmetric top, we have noted that the unresolved CIDs for a vibrational band obtained by summing over all allowed states and then averaging over the initial states are identical to the CIDs for an isotropic fluid. To prove this identity for the symmetric top, we made use of some of the properties of the factors $D^k_{J'K',JK}$ given by (1.20) which appear in the fully developed intensity factor expression (1.19) to show that summing these intensity factors over all allowed final states gives a simple result independent of initial state. For the general case of an asymmetric top, it is easier to work with the original definition of an intensity factor (2.12) rather than the finalised form (2.16).

We may write [31]

$$\begin{aligned}
\sum_{J'\mathcal{T}'}[I^k_q(TS)]_{n'J'\mathcal{T}'M',nJ\mathcal{T}M} &= \frac{1}{(2J+1)}\sum_{MM'J'\mathcal{T}'}\langle n', J'\mathcal{T}'M' \mid \hat{T}^k_q \mid n, J\mathcal{T}M\rangle \\
&\quad \times\langle n', J'\mathcal{T}'M' \mid \hat{S}^k_q \mid n, J\mathcal{T}M\rangle^* \\
&= \frac{1}{(2k+1)(2J+1)}\sum_{MM'J'\mathcal{T}'qq'}\langle n' \mid \hat{T}^k_{q'} \mid n\rangle \\
&\quad \times\langle n' \mid \hat{S}^k_{q'} \mid n\rangle^* \\
&\quad \times\langle J'\mathcal{T}'M' \mid D^k_{q'q}(\omega) \mid J\mathcal{T}M\rangle \\
&\quad \times\langle J'\mathcal{T}'M' \mid D^k_{q'q}(\omega) \mid J\mathcal{T}M\rangle^* \\
&= \frac{1}{(2k+1)}\sum_{q'}\langle n' \mid \bar{T}^k_{q'} \mid n\rangle\langle n' \mid \bar{S}^k_{q'} \mid n\rangle^* \qquad (2.21)
\end{aligned}$$

where the unitarity of the matrix of finite rotations is employed in the final step. Clearly, the development is also applicable to the symmetric top for which $\mathcal{T} = K$. By correlating intensity factors with each term $\hat{S}^k_q\hat{T}^{k*}_q$ appearing in the CIDs in the usual manner, this result allows us to prove the required equivalence for a general molecule.

2.3 Discussion

It may be seen from table 2.1 and from the explicitly calculated dimensionless CIDs of subsection 2.2.3 that the rotational selection rules for each of the tensor components, with the exception of $\bar{T}^2_0$ and $\bar{T}^2_2 + \bar{T}^2_{-2}$, are different. A consequence of this is the simple temperature independent dimensionless CIDs obtained for individual transitions except those associated with tensor components $\overline{T}^2_0$ and $\overline{T}^2_2 + \overline{T}^2_{-2}$.

It is possible to show that the CIDs for individual transitions in the symmetric top may be recovered from (2.17) to (2.20) by retaining only one of the coefficients a^{JT}_K per state for both initial and final states and setting it to unity. Clearly ΔK is restricted to one value as a result and the appearance of one of the tensor components $\overline{T}^2_0$ and $\overline{T}^2_2 + \overline{T}^2_{-2}$ in the CIDs for a given transition precludes the appearance of the other. It is also necessary to note that levels which form distinct non-degenerate pairs of opposite parity in the asymmetric top, coalesce in the limiting case of the symmetric top. We must therefore sum the relevant intensity contributions to take account of this degeneracy and correctly reproduce the results of chapter one for the symmetric top. This is effected by adding intensity contributions associated with $\overline{T}^2_{q'} + \overline{T}^2_{-q'}$ to contributions associated with $\overline{T}^2_{q'} - \overline{T}^2_{-q'}$.

In chapter one, it was noted that a group polarizability calculation of the pure rotational ROA in triphenylborane had been carried out [10] and it should be mentioned that we have attempted some more complicated group polarizability calculations of the pure rotational ROA in epoxypropane and *trans*-2,3-epoxybutane within the accidentally symmetric top approximation. Slight variation in the group polarizability isotropies and anisotropies used was found to effect a large change in the magnitude, and even in the sign, of the calculated CIDs. Since the starting data was in itself unreliable, as several quite different values were available in the literature for each group polarizability component required, it was decided that the results did not merit inclusion. However, the calculations did highlight the artificiality of

splitting a molecule up into independent groups.

Although in this chapter and the preceding one, the theory of rotational ROA has been set out in some detail, an experimental investigation remains an interesting project for the future. The requirements and possible difficulties of such an investigation in relation to conventional gas phase Raman spectroscopy should, however, be mentioned. Obtaining sufficient spectral resolution is a familiar problem in conventional gas phase Raman spectroscopy which is particularly pertinent for structures complex enough to be chiral. In recent years, workers have been able to avail themselves of a range of techniques associated with non-linear Raman spectroscopy such as coherent anti-Stokes Raman spectroscopy (CARS), Raman gain and inverse Raman spectroscopy which provide resolution orders of magnitude higher than that obtainable with linear Raman spectroscopy [43]. Indeed, the theory of CARS ROA and magnetic CARS ROA has been developed [44]. Unfortunately, one of the main disadvantages of CARS is a high non-resonant background leading to a poor signal-to-noise ratio and thus limiting detectability. It was probably for this reason that attempts to observe natural and magnetic CARS ROA proved unsuccessful [44]. However, as we have seen it is often the case that information which is a function of handedness and given uniquely by ROA does not depend on complete spectral resolution.

Chapter 3

Circular dichroism and optical rotation

3.1 Introduction

A detailed treatment of optical rotation in symmetric tops which takes account of quantised molecular rotation has already been given by Chui [6]. We propose an alternative development which is nevertheless consistent with the earlier work and introduces the trivial modification of accommodating optical rotation at absorbing frequencies and rotational CD by allowing for the finite lifetime of the excited virtual states. Our results are then generalised to encompass the asymmetric top. Finally, we explore optical rotation associated with purely rotational transitions which requires a rotation-induced magnetic moment.

3.2 Theory

3.2.1 The symmetric top

The angle of optical rotation for a collection of freely rotating symmetric tops is [1,45]

$$\begin{aligned}\Delta\Theta \;\approx\; & -\frac{1}{2\mathcal{Z}}\omega\mu_o\ell N\sum_{JKM}\frac{g_{JK}}{(2J+1)} \\ & \times\left[\frac{1}{3}\omega(A_{xyz}(f)-A_{yxz}(f))+G'_{xx}(f)+G'_{yy}(f)\right]e^{-E_{JK/kT}} \qquad (3.1)\end{aligned}$$

where $\mathcal{Z}$ is the rotational partition function, ω is the frequency of the incident light, ℓ is the path length and N is the molecule number density. We have also introduced the dispersion lineshape function f [1] and the dispersive parts of the optical activity tensors $G'_{\alpha\beta}(f)$ and $A_{\alpha\beta\gamma}(f)$ defined by

$$\begin{aligned}G'_{\alpha\beta}(f) = & -\frac{2}{\hbar}\sum_{n'J'K'M'} f\omega \\ & \times\mathrm{Im}(\langle n,JKM\mid\mu_\alpha\mid n',J'K'M'\rangle\langle n',J'K'M'\mid m_\beta\mid n,JKM\rangle) \qquad (3.2)\\ A_{\alpha\beta\gamma}(f) = & \frac{2}{\hbar}\sum_{n'J'K'M'} f\omega_{n'J'K',nJK} \\ & \times\mathrm{Re}(\langle n,JKM\mid\mu_\alpha\mid n',J'K'M'\rangle\langle n',J'K'M'\mid\Theta_{\beta\delta}\mid n,JKM\rangle) \qquad (3.3)\end{aligned}$$

The contribution to $\Delta\Theta$ from $G'_{xx}(f)+G'_{yy}(f)$ for a molecule in rotational state $|JKM\rangle$ is

$$\begin{aligned}(2J+1)^{-1}\sum_M(G'_{xx}(f)+G'_{yy}(f)) \;=\; & \frac{2}{\hbar}(2J+1)^{-1}\sum_{n'J'K'M'M} f\omega \\ & \times\mathrm{Im}(\langle n,JKM\mid\mu^1_1\mid n',J'K'M'\rangle \\ & \times\langle n',J'K'M'\mid m^1_{-1}\mid n,JKM\rangle \\ & +\langle n,JKM\mid\mu^1_{-1}\mid n',J'K'M'\rangle \\ & \times\langle n',J'K'M'\mid m^1_1\mid n,JKM\rangle) \\ = \; & \frac{2}{\hbar}\sum_{n',J'K'M'M} f\omega(2J'+1)(-1)^{K+K'+1}\end{aligned}$$

$$
\begin{aligned}
&\times \begin{pmatrix} J & J' & 1 \\ K & -K' & -K+K' \end{pmatrix}^2 \\
&\times \left[\begin{pmatrix} J & J' & 1 \\ M & -M' & -1 \end{pmatrix}^2 + \begin{pmatrix} J & J' & 1 \\ -M & M' & -1 \end{pmatrix}^2 \right] \\
&\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n' \rangle \langle n' \mid \overline{m^1_{K'-K}} \mid n \rangle) \\
= \; & \frac{4}{3\hbar} \sum_{n'J'K'} f\omega (2J'+1)(-1)^{K+K'+1} \\
&\times \begin{pmatrix} J & J' & 1 \\ K & -K' & -K+K' \end{pmatrix}^2 \\
&\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n' \rangle \langle n' \mid \overline{m^1_{K'-K}} \mid n \rangle) \qquad (3.4)
\end{aligned}
$$

where the second step involves application of the Wigner-Eckart theorem for axially symmetric systems (1.19) and the third step exploits the orthogonality relations of the $3-j$ symbols. Note that we have taken account of the $(2J+1)$ degeneracy of the M substates.

Similarly for the contribution from $A_{xyz}(f) - A_{yxz}(f)$:

$$
\begin{aligned}
&(2J+1)^{-1} \sum_M A_{xyz}(f) - A_{yxz}(f) = \\
&\quad \frac{\sqrt{2}}{\hbar} (2J+1)^{-1} \sum_{n'J'K'M'M} f\omega_{n'J'K',nJK} \\
&\quad \times \mathrm{Im}(\langle n, JKM \mid \mu^1_1 \mid n', J'K'M' \rangle \\
&\quad \times \langle n', J'K'M' \mid \Theta^2_{-1} \mid n, JKM \rangle \\
&\quad - \langle n, JKM \mid \mu^1_{-1} \mid n', J'K'M' \rangle \\
&\quad \times \langle n', J'K'M' \mid \Theta^2_1 \mid n, JKM \rangle) \\
= \; & \frac{\sqrt{2}}{\hbar} \sum_{n'J'K'M'M} f\omega_{n'J'K',nJK} (-1)^{K+K'+1} (2J'+1) \\
&\quad \times \begin{pmatrix} J & J' & 1 \\ K & -K' & K'-K \end{pmatrix} \begin{pmatrix} J & J' & 2 \\ K & -K' & K'-K \end{pmatrix} \\
&\quad \times \left[\begin{pmatrix} J & J' & 1 \\ M & -M' & -1 \end{pmatrix} \begin{pmatrix} J & J' & 2 \\ M & -M' & -1 \end{pmatrix} \right.
\end{aligned}
$$

$$- \left(\begin{array}{ccc} J & J' & 1 \\ M & -M' & 1 \end{array} \right) \left(\begin{array}{ccc} J & J' & 2 \\ M & -M' & 1 \end{array} \right) \Bigg]$$
$$\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n' \rangle \langle n' \mid \overline{\Theta^2_{K'-K}} \mid n \rangle) \tag{3.5}$$

However, the orthogonality properties of the $3-j$ symbols dictate that summation over M and M' produces a zero result, which means that there is no contribution from $A_{xyz}(f) - A_{yxz}(f)$.

Thus, we finally obtain

$$\Delta\Theta \approx \frac{2\omega^2 \mu_o \ell N}{3\hbar \mathcal{Z}} \sum_{\substack{JK \\ n'J'K'}} f g_{JK} (2J'+1)(-1)^{K+K'} \left(\begin{array}{ccc} J & J' & 1 \\ K & -K' & -K+K' \end{array} \right)^2$$
$$\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n' \rangle \langle n' \mid \overline{m^1_{K'-K}} \mid n \rangle) e^{-E_{JK}/kT} \tag{3.6}$$

It is then immediately possible to write the following result for CD:

$$\eta \approx \frac{2\omega^2 \mu_o \ell N}{3\hbar \mathcal{Z}} \sum_{\substack{JK \\ n'J'K'}} g g_{JK} (2J'+1)(-1)^{K+K'} \left(\begin{array}{ccc} J & J' & 1 \\ K & -K' & -K+K' \end{array} \right)^2$$
$$\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n' \rangle \langle n' \mid \overline{m^1_{K'-K}} \mid n \rangle) e^{-E_{JK}/kT} \tag{3.7}$$

where η is the macroscopic ellipticity, obtained from (3.6) simply by replacement of the dispersion lineshape function f by the absorption lineshape function g [1]. Expression (3.6) is in agreement with Chui's more rigorous result which involves a summation over all ranks of interference terms between electric and magnetic multipoles of the same rank [6], while our result depends on a single electric dipole-magnetic dipole term. For most purposes our expression is adequate because the dipole-dipole term dominates strongly over the other terms in the summation [46].

We may split the summations in (3.6) and (3.7) into two parts corresponding to $n' = n$ and $n' \neq n$. Thus, (3.6), for example, becomes

$$\Delta\Theta \approx \frac{2\omega^2 \mu_o \ell N}{3\hbar \mathcal{Z}} \left[\sum_{\substack{JK \\ J'K'}} f g_{JK} (2J'+1)(-1)^{K+K'} \left(\begin{array}{ccc} J & J' & 1 \\ K & -K' & -K+K' \end{array} \right)^2 \right.$$
$$\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n \rangle \langle n \mid \overline{m^1_{K'-K}} \mid n \rangle) e^{-E_{JK}/kT}$$

$$+\sum_{\substack{JK\\J'K'\\n'\neq n}} fg_{JK}(2J'+1)(-1)^{K+K'}\begin{pmatrix} J & J' & 1 \\ K & -K' & -K+K' \end{pmatrix}^2$$

$$\times \mathrm{Im}(\langle n \mid \overline{\mu^1_{K-K'}} \mid n'\rangle\langle n' \mid \overline{m^1_{K'-K}} \mid n\rangle)e^{-E_{JK}/kT}\Bigg] \tag{3.8}$$

The first term describes the contribution to optical rotation through purely rotational excited states while the second term describes the contribution through rovibronic excited states. It is appropriate to consider the first term at rotational transition frequencies, that is, in the microwave region and the second term at the higher frequencies characteristic of vibrational or electronic transitions. The first term, dependent on purely rotational virtual states, is equal to zero because it is always possible in the absence of an external source of time asymmetry, such as a magnetic field, to construct molecular states for which the expectation value of the magnetic dipole operator is zero since it is a Hermitian time-odd operator [1]. There is thus no optical rotation in the microwave region or, for identical reasons, CD analog to pure rotational ROA, within the approximation used in this derivation. The second term may be further separated into a part which is a function of purely rovibrational transitions dominant in the middle and far infrared regions and a part which is a function of rovibronic transitions dominant in the near infrared, visible and ultraviolet regions [1].

3.2.2 The asymmetric top

We have shown in chapter two how a treatment of rotational ROA in symmetric tops provides a framework on which to build the more sophisticated theory required for an asymmetric top. In an analogous fashion, it is possible to extend the optical rotation results obtained for a symmetric top to an asymmetric top. We develop (3.1) making use of definitions (3.2) and (3.3) suitably modified for the asymmetric

top by replacing the K quantum number of the symmetric top rotational state by the pseudo-quantum number $\mathcal{T}$ for the asymmetric top rotational state. It may be shown using (2.15) for rotational matrix elements of asymmetric tops that

$$
\begin{aligned}
\Delta\Theta \approx\ & \frac{2\omega^2\mu_o\ell N}{3\hbar\mathcal{Z}} \sum_{\substack{J\mathcal{T} \\ n'J'\mathcal{T}'}} f g_{J\mathcal{T}}(2J'+1) \\
& \times \mathrm{Im}\Bigg[\Bigg\{ \sum_{K=0}^{J} \frac{(-1)^K}{2} \langle n \mid \overline{\mu_0^1} \mid n' \rangle \\
& \times [1-(-1)^{J+J'}(-1)^{\gamma+\gamma'}] a_K^{J\mathcal{T}} a_K^{J'\mathcal{T}'} \begin{pmatrix} J & 1 & J' \\ -K & 0 & K \end{pmatrix} \\
& -i \sum_{K=1}^{J} [\langle n \mid \overline{\mu_1^1} \mid n' \rangle + (-1)^{J+J'}(-1)^{\gamma+\gamma'} \langle n \mid \overline{\mu_{-1}^1} \mid n' \rangle] \\
& \times \Bigg[\frac{(-1)^{\gamma'+1}}{\sqrt{2}} a_o^{J\mathcal{T}} a_1^{J'\mathcal{T}'} \begin{pmatrix} J & 1 & J' \\ 0 & 1 & -1 \end{pmatrix} + \frac{1}{\sqrt{2}} a_1^{J\mathcal{T}} a_o^{J'\mathcal{T}'} \begin{pmatrix} J & 1 & J' \\ -1 & 1 & 0 \end{pmatrix} \\
& + \frac{(-1)^{K-1}}{2} a_K^{J\mathcal{T}} a_{K-1}^{J'\mathcal{T}'} \begin{pmatrix} J & 1 & J' \\ -K & 1 & K-1 \end{pmatrix} \\
& + \frac{(-1)^{1-K+\gamma'}}{2} a_K^{J\mathcal{T}} a_{1-K}^{J'\mathcal{T}'} \begin{pmatrix} J & 1 & J' \\ -K & 1 & K-1 \end{pmatrix} \\
& + \frac{(-1)^{K+1+\gamma+\gamma'}}{2} a_K^{J\mathcal{T}} a_{K+1}^{J'\mathcal{T}'} \begin{pmatrix} J & 1 & J' \\ K & 1 & -K-1 \end{pmatrix} \Bigg] \Bigg\} \\
& \times \Bigg\{ \sum_{K=0}^{J} \frac{(-1)^K}{2} \langle n' \mid \overline{m_0^1} \mid n \rangle \\
& \times [1-(-1)^{J+J'}(-1)^{\gamma+\gamma'}] a_K^{J\mathcal{T}} a_K^{J'\mathcal{T}'} \begin{pmatrix} J' & 1 & J \\ -K & 0 & K \end{pmatrix} \\
& -i \sum_{K=1}^{J} [\langle n' \mid \overline{m_1^1} \mid n \rangle + (-1)^{J+J'}(-1)^{\gamma+\gamma'} \langle n' \mid \overline{m_{-1}^1} \mid n \rangle] \\
& \times \Bigg[\frac{(-1)^{\gamma+1}}{\sqrt{2}} a_1^{J\mathcal{T}} a_o^{J'\mathcal{T}'} \begin{pmatrix} J' & 1 & J \\ 0 & 1 & -1 \end{pmatrix}
\end{aligned}
$$

$$+\frac{1}{\sqrt{2}}a_o^{JT}a_1^{J'T'}\begin{pmatrix} J' & 1 & J \\ -1 & 1 & 0 \end{pmatrix}+\frac{(-1)^K}{2}a_K^{JT}a_{K+1}^{J'T'}\begin{pmatrix} J' & 1 & J \\ -K-1 & 1 & K \end{pmatrix}$$

$$+\frac{(-1)^{K+\gamma}}{2}a_K^{JT}a_{1-K}^{J'T'}\begin{pmatrix} J' & 1 & J \\ K-1 & 1 & -K \end{pmatrix}$$

$$+\frac{(-1)^{K+\gamma+\gamma'}}{2}a_K^{JT}a_{K-1}^{J'T'}\begin{pmatrix} J' & 1 & J \\ K-1 & 1 & -K \end{pmatrix}\Bigg]\Bigg\}\Bigg]e^{-E_{JT/kT}} \tag{3.9}$$

The combination $A_{xyz}(f)-A_{yxz}(f)$ does not contribute because, as for the symmetric top, summation over M and M' leads to a zero result. Again, if the dispersion lineshape function f is replaced by the absorption lineshape function g in (3.9), the expression for η is obtained.

3.2.3 Optical rotation in the high frequency limit

At high frequencies of incident light, we can introduce a version of the Placzek approximation as discussed in subsection 1.2.1 such that

$$G'_{\alpha\beta}=\langle n_v n_r \mid G'_{\alpha\beta}(Q) \mid n_v n_r\rangle \tag{3.10}$$

Note that we have dropped the dependence on lineshape function as it is implicit in the approximation that we are considering off-resonance conditions. We can now use (3.10) to derive an approximate expression for optical rotation. Assuming the conditions necessary for Placzek's approximation we write

$$\begin{aligned} G'_{xx}-G'_{yy}+\frac{1}{3}\omega(A_{xyz}-A_{yxz}) &= \langle n,JTM \mid -\frac{i}{3}\omega A_0^2-\sqrt{\frac{2}{3}}G_0'^2 \mid n,JTM\rangle \\ &\quad -\frac{2}{\sqrt{3}}\langle n,JTM \mid G_0'^0 \mid n,JTM\rangle \end{aligned} \tag{3.11}$$

where $\mathcal{T}=K$ for the symmetric top.

Only the dependence of the matrix elements on M can be split off in general

[33,34], so that (3.11) becomes, in terms of reduced matrix elements

$$\begin{aligned} G'_{xx} - G'_{yy} + \frac{1}{3}\omega(A_{xyz} - A_{yxz}) &= (-1)^{J-M+1} \begin{pmatrix} J & 2 & J \\ -M & 0 & M \end{pmatrix} \\ &\times \langle n, JT \parallel -\frac{i}{3}\omega A^2 - \sqrt{\frac{2}{3}} G'^2 \parallel n, JT \rangle \\ &- \frac{2}{\sqrt{3}}(-1)^{J-M} \begin{pmatrix} J & 0 & J \\ -M & 0 & M \end{pmatrix} \\ &\times \langle n, JT \parallel G'^0 \parallel n, JT \rangle \end{aligned} \tag{3.12}$$

Summation over M of the first term in (3.12) gives zero since [27,47]

$$\begin{pmatrix} J & 2 & J \\ -M & 0 & M \end{pmatrix} = \frac{(-1)^{J+M}[3M^2 - J(J+1)]}{[J(J+1)(2J+3)(2J+1)(2J-1)]^{\frac{1}{2}}} \tag{3.13}$$

$$\sum_{M=-J}^{J} M^2 = \frac{1}{3}(2J+1)J(J+1) \tag{3.14}$$

and each rotational state is $(2J+1)$ degenerate in M. Thus our final expression is

$$\Delta\Theta \approx -\frac{1}{3}\omega\mu_o \ell N G'_{\alpha\alpha} \tag{3.15}$$

It should be noted that, within the approximations made here, $\Delta\Theta$ is independent of rotational state and thus temperature, and coincides with the well-known classical result for optical rotation in an isotropic sample [1].

3.2.4 Optical rotation at microwave frequencies

Thus far we have only taken account of the contribution from electrons to the magnetic moment in the molecule-fixed frame and have ignored the effect of molecular rotation on the resultant space-fixed magnetic moment. Within this approximation there is no optical rotation in the region of pure rotational transitions. However, Salzman has pointed out that optical activity at microwave frequencies is, in principle, possible and depends on a rotation-induced magnetic moment which

contains contributions from both electrons and nuclei [8,9]. The necessary theory has been developed to describe the effect for an accidentally symmetric top in rotational state $|n, JKM\rangle = |n, 000\rangle$ [8]. The mass distribution of this top is that of a symmetric top but the molecular g tensor is not diagonal in the principal axes frame.

We can accommodate the effect of molecular rotation in our formulation of optical rotation by employing matrix elements in which the magnetic dipole operator operates on rotational states [48,49]. Following Salzman, we consider specifically the $J = 0$ to $J = 1$ transition of the accidentally symmetric top. The required matrix elements are given by Salzman [8,9] and reproduced in table 3.1. (The tabulated matrix elements are expressed in Cartesian notation as are Salzman's results, so we do not attempt a translation into spherical tensor form.)

By making use of table 3.1, we may write

$$\mathrm{Im}(G'_{xx} + G'_{yy}) = -\frac{2\mu_N\left[\mu_X(g_{YZ} - g_{ZY}) + \mu_Y(g_{ZX} - g_{XZ}) + \mu_Z(g_{XY} - g_{YX})\right]}{3\hbar(\omega_{10}^2 - \omega^2)} \tag{3.16}$$

where we have assumed off-resonance conditions to ensure that we may neglect the energy differences in the K sublevels.

Noting that Salzman's molecular β parameter is related to $G'_{\alpha\beta}$ as follows:

$$\beta = -\frac{\lambda G'_{\alpha\alpha}}{6\pi} \tag{3.17}$$

it is possible to see that (3.16) is consistent with (21) of Salzman's paper [8]. Moreover, the derivation presented here constitutes a much more direct method of calculating an optical rotatory parameter in the microwave region.

3.3 Discussion

It is interesting to note that prior to the work of Salzman, an independent treatment of optical activity was presented by Atkins in which individual rotational

Table 3.1

Rotational matrix elements of μ_x, μ_y, m_x and m_y for the $J = 0$ to $J = 1$ transition of the accidentally symmetric top, where $g_{\alpha\beta}$ is the molecular g tensor and μ_N is the nuclear magneton [8].

Space-fixed matrix elements	Molecule-fixed matrix elements
$\langle n, 11 \pm 1 \mid \mu_x \mid n, 000 \rangle$	$\pm\frac{1}{2\sqrt{3}}(\mu_X + i\mu_Y)$
$\langle n, 10 \pm 1 \mid \mu_x \mid n, 000 \rangle$	$\mp\frac{1}{\sqrt{6}}\mu_Z$
$\langle n, 1-1 \pm 1 \mid \mu_x \mid n, 000 \rangle$	$\mp\frac{1}{2\sqrt{3}}(\mu_X - i\mu_Y)$
$\langle n, 11 \pm 1 \mid \mu_y \mid n, 000 \rangle$	$-\frac{i}{2\sqrt{3}}(\mu_X + i\mu_Y)$
$\langle n, 10 \pm 1 \mid \mu_y \mid n, 000 \rangle$	$\frac{i}{\sqrt{6}}\mu_Z$
$\langle n, 1-1 \pm 1 \mid \mu_y \mid n, 000 \rangle$	$\frac{i}{2\sqrt{3}}(\mu_X - i\mu_Y)$
$\langle n, 11 \pm 1 \mid m_x \mid n, 000 \rangle$	$\frac{\pm i\mu_N}{4\sqrt{3}}[g_{YZ} - g_{ZY} + i(g_{ZX} - g_{XZ})]$
$\langle n, 10 \pm 1 \mid m_x \mid n, 000 \rangle$	$\frac{\mp i\mu_N}{2\sqrt{6}}(g_{XY} - g_{YX})$
$\langle n, 1-1 \pm 1 \mid m_x \mid n, 000 \rangle$	$\frac{\mp i\mu_N}{4\sqrt{3}}[g_{YZ} - g_{ZY} - i(g_{ZX} - g_{XZ})]$
$\langle n, 11 \pm 1 \mid m_y \mid n, 000 \rangle$	$\frac{\mu_N}{4\sqrt{3}}[g_{YZ} - g_{ZY} + i(g_{ZX} - g_{XZ})]$
$\langle n, 10 \pm 1 \mid m_y \mid n, 000 \rangle$	$-\frac{\mu_N}{2\sqrt{6}}(g_{XY} - g_{YX})$
$\langle n, 1-1 \pm 1 \mid m_y \mid n, 000 \rangle$	$-\frac{\mu_N}{4\sqrt{3}}[g_{YZ} - g_{ZY} - i(g_{ZX} - g_{XZ})]$

states were explicitly considered and a novel manifestation of optical rotation predicted, with molecular rotation again cited as a prerequisite [50]. However, the underlying symmetry characteristics of this effect are completely different to those of optical rotation in the microwave region as proposed by Salzman [14,39].

The optical rotation of the earlier study is associated with the difference in response to circularly polarized light shown by counter-rotating molecules and is properly classified as a magnetic optical activity phenomenon. The magnetic optical rotation observable is generated by a time-odd, even-parity operator and it is therefore supported by states which do not have definite reversality. Suitable states are provided by molecular rotational states of definite angular momentum. Notice that an equilibrium ensemble can be thought of as containing equal numbers of counter-rotating molecules. Consequently, there would be no overall rotation of plane polarized light by a bulk sample unless it were in the presence of an external time-odd influence such as a magnetic field which, in breaking the time-reversal symmetry of the system, would lift the degeneracy of counter-rotating molecules. The effect described by Salzman is an example of natural optical activity. The time-even, odd-parity operator which generates the natural optical rotation observable is supported exclusively by the mixed parity internal states of a chiral molecule. As expected, the combination of tensorial components in (3.16) describing molecular rotation-induced natural optical activity may only be non-zero for a chiral molecule.

It is finally important to ask which of the expressions calculated in this chapter are likely to be most useful from an experimental viewpoint. Since rotational structure has already been seen in gas phase vibrational IRCD spectra, this could prove a favourable choice for a more detailed study [51]. The expressions appropriate to an analysis of such spectra are (3.7) for symmetric tops and its analog for asymmetric tops obtainable from (3.9). Experimental verification of natural optical rotation in the microwave region is hampered by two intrinsic limiting factors. First, the angle of rotation decreases as the frequency of the impinging light decreases, and second,

the contributing magnetic dipole matrix elements are about 10^{-3} times smaller than elements associated with electronic spin or orbital angular momenta.

Part II

Discrimination in the dispersion interaction between odd-electron chiral molecules

Chapter 4

Semi-classical development

4.1 Introduction

The interaction of one chiral molecule with another, not necessarily of the same chemical species, is determined by the relative handedness of the pair. This is manifest in numerous diverse physical phenomena ranging from the difference in melting points between active and racemic crystalline forms of a compound to biological systems in which physiological activity is linked to one stereoisomer exclusively [52]. Various model mechanisms have been posited to rationalise the discriminatory behaviour displayed by coupled chiral molecules for disparate chemical environments and physical conditions [2,52-58].

Our specific objective is to shed new light on an old topic, namely that of the difference in the dispersion interaction between a pair of chemically identical molecules of the same and opposite absolute configurations.

The possibility of a term discriminating between like and unlike pairs of chiral molecules in the dispersion interaction energy was first suggested by Mavroyannis and Stephen [53]. Their calculation treated the case of an interaction averaged over all relative orientations of the two molecules. Later work carried out by Craig,

Power and Thirunamachandran amplified the original idea, extending the previous results to cover locked and semi-locked molecular configurations [54,55].

The development presented here considers additional contributions to both discriminatory and non-discriminatory dispersion interactions between chiral molecules in degenerate states. Doubly degenerate Kramers conjugate states of odd-electron molecules, being the simplest and most common example, are discussed in detail. By allowing for degeneracy the possibility of contributions which are a function of time-odd tensor components is introduced [1,59]. This augments the commonly cited time-even contributions. Buckingham and Joslin have discussed spin-dependent dispersion forces between alkali metal atoms originating in time-odd property and transition polarizability tensors. The resulting contribution to the overall dispersion interaction energy was found to be negligibly small [60]. However, the work does provide impetus for a similar investigation of possible novel terms in the discriminatory dispersion interaction dependent on time-odd components of the complex optical activity tensor $\tilde{G}_{\alpha\beta}$.

In this chapter a semi-classical development of the discriminatory dispersion interaction applicable at intermolecular separations in the near-zone region is given along with a model calculation on a hypothetical chiral odd-electron transition metal complex of symmetry O^*.

4.2 Theory

4.2.1 A semi-classical development of the dispersion interaction for the near-zone limit

We present a semi-classical treatment of the discriminatory and non-discriminatory parts of the dispersion interaction for the near-zone limit. The near-zone is that intermediate region in which the molecules are sufficiently distanced, one from the

other, to allow electron exchange interactions to be neglected, yet near enough that retardation effects need not be taken into account [61]. Since in this range the indistinguishability of electrons is irrelevant, we write the total wavefunction of the two-molecule system as a simple product of the wavefunctions of the isolated molecules 1 and 2.

The interaction Hamiltonian may be written [54,55]

$$H_{int} = H_E + H_M \tag{4.1}$$

where H_E and H_M in the dipole approximation are given by

$$H_E = -\frac{1}{4\pi\epsilon_o} T_{\alpha\beta}\mu_{1_\alpha}\mu_{2_\beta} \tag{4.2}$$

$$H_M = -\frac{\mu_o}{4\pi} T_{\alpha\beta} m_{1_\alpha} m_{2_\beta} \tag{4.3}$$

where

$$T_{\alpha\beta} = \nabla_\alpha \nabla_\beta R^{-1} = (3R_\alpha R_\beta - R^2\delta_{\alpha\beta})R^{-5} \tag{4.4a}$$

with $\mathbf{R} = \mathbf{R}_{21}$, the position vector of molecule 2 relative to molecule 1. The electric dipole moment μ_α is given by (1.5a) and

$$m_\alpha = \sum_i \frac{e_i}{2m_i}(l_{i_\alpha} + g_i s_{i_\alpha}) \tag{4.4b}$$

is the magnetic dipole moment for the collection of charges e_i with mass m_i, orbital and spin angular momenta l_{i_α} and s_{i_α} and g-factor g_i. Notice that (4.4b) is a generalisation of (1.5b) which allows for a contribution to the magnetic dipole moment from spin angular momentum s.

It is possible to extend the interaction potentials to include higher order multipolar terms, but the associated contributions to the total dispersion energy attenuate more rapidly with increasing intermolecular separation than the dipole-dipole parts, and are not discussed here [46,62]. However, it is interesting to note that new discriminatory contributions, some of which originate in pure electrostatic interactions, are yielded by more sophisticated treatments of this type [46]. We shall

consider the non-discriminatory dispersion energy arising purely from an electric dipole-electric dipole electrostatic interaction and the discriminatory part resulting from an electric dipole-magnetic dipole interaction.

Initially we derive expressions to describe the perturbation Hamiltonian matrix elements for molecule 1 with isoenergetic states $|n_1\rangle$ and $|m_1\rangle$ and molecule 2 with isoenergetic states $|n_2\rangle$ and $|m_2\rangle$. The eigenvalues of the secular matrix in the particular case of odd-electron molecules in twofold degenerate Kramers states are then explicitly given.

4.2.2 The non-discriminatory dispersion energy

Considering only H_E as the perturbation Hamiltonian, we find from second-order perturbation theory [60,62]

$$\begin{aligned} E_{m_1m_2,n_1n_2} &= -\frac{1}{16\pi^2\epsilon_o^2}T_{\alpha\beta}T_{\gamma\delta} \\ &\times \sum_{\substack{j_1\neq n_1,m_1 \\ j_2\neq n_2,m_2}} \frac{\langle m_1m_2 \mid \mu_{1_\alpha}\mu_{2_\beta} \mid j_1j_2\rangle\langle j_1j_2 \mid \mu_{1_\gamma}\mu_{2_\delta} \mid n_1n_2\rangle}{\hbar(\omega_{j_1n_1}+\omega_{j_2n_2})} \end{aligned} \tag{4.5}$$

The above expression can be written in terms of the dynamic transition polarizabilities of the individual molecules. Making use of the identities

$$\begin{aligned} \frac{1}{A+B} &= \frac{2}{\pi}\int_0^\infty \frac{AB}{(A^2+u^2)(B^2+u^2)}du \\ &= \frac{2}{\pi}\int_0^\infty \frac{u^2}{(A^2+u^2)(B^2+u^2)}du \end{aligned} \tag{4.6}$$

with $A>0$, $B>0$,

we obtain

$$\begin{aligned} E_{m_1m_2,n_1n_2} &= -\frac{\hbar}{32\pi^3\epsilon_o^2}T_{\alpha\beta}T_{\gamma\delta} \\ &\times \int_0^\infty \Big[(\tilde{\alpha}_{1_{\alpha\gamma}})^+_{m_1n_1}(iu)(\tilde{\alpha}_{2_{\beta\delta}})^+_{m_2n_2}(iu) \\ &-(\tilde{\alpha}_{1_{\alpha\gamma}})^-_{m_1n_1}(iu)(\tilde{\alpha}_{2_{\beta\delta}})^-_{m_2n_2}(iu)\Big]\,du \end{aligned} \tag{4.7}$$

where we have introduced dynamic transition polarizabilities [1,60,62]

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{+}_{mn}(\omega) &= \frac{1}{\hbar}\sum_{j\neq n,m}\frac{\omega_{jn}}{\omega_{jn}^2-\omega^2} \\
&\quad\times\left(\langle m\mid\mu_\alpha\mid j\rangle\langle j\mid\mu_\beta\mid n\rangle+\langle m\mid\mu_\beta\mid j\rangle\langle j\mid\mu_\alpha\mid n\rangle\right) \\
&= (\tilde{\alpha}_{\beta\alpha})^{+}_{mn}(\omega) \qquad (4.8a)
\end{aligned}
$$

$$
\begin{aligned}
(\tilde{\alpha}_{\alpha\beta})^{-}_{mn}(\omega) &= \frac{1}{\hbar}\sum_{j\neq n,m}\frac{\omega}{\omega_{jn}^2-\omega^2} \\
&\quad\times\left(\langle m\mid\mu_\alpha\mid j\rangle\langle j\mid\mu_\beta\mid n\rangle-\langle m\mid\mu_\beta\mid j\rangle\langle j\mid\mu_\alpha\mid n\rangle\right) \\
&= -(\tilde{\alpha}_{\beta\alpha})^{-}_{mn}(\omega) \qquad (4.8b)
\end{aligned}
$$

which may be obtained from transition polarizabilities (1.7) by particularising to degenerate initial and final states. Note that we have explicitly written these transition tensors as functions of ω to emphasize that they are dynamic, as it will be necessary later to distinguish between *dynamic* and *static* transition tensors.

A similar analysis is possible for a purely magnetic interaction with H_M as the perturbation Hamiltonian. The resulting contribution differs from (4.5) only in that the μ_α are replaced by m_α and the constant factor is appropriately modified. Magnetic transition dipoles are characteristically two or three orders of magnitude smaller than electric transition dipoles. The purely magnetic contribution is therefore negligible in comparison.

4.2.3 Discriminatory dispersion energy

From the cross term of H_E and H_M, we obtain a discriminatory contribution for chiral molecules as follows[54,55]:

$$
\begin{aligned}
E'_{m_1m_2,n_1n_2} &= -\frac{\mu_o}{16\pi^2\epsilon_0}T_{\alpha\beta}T_{\gamma\delta}\sum_{\substack{j_1\neq n_1,m_1\\ j_2\neq n_2,m_2}}\left\{\frac{1}{\hbar(\omega_{j_1n_1}+\omega_{j_2n_2})}\right. \\
&\quad\times\left(\langle m_1m_2\mid\mu_{1_\alpha}\mu_{2_\beta}\mid j_1j_2\rangle\langle j_1j_2\mid m_{1_\gamma}m_{2_\delta}\mid n_1n_2\rangle\right. \\
&\quad\left.\left.+\langle m_1m_2\mid m_{1_\gamma}m_{2_\delta}\mid j_1j_2\rangle\langle j_1j_2\mid\mu_{1_\alpha}\mu_{2_\beta}\mid n_1n_2\rangle\right)\right\} \qquad (4.9)
\end{aligned}
$$

Again using identities (4.6) we find

$$E'_{m_1m_2,n_1n_2} = -\frac{\mu_o\hbar}{16\pi^3\epsilon_o}T_{\alpha\beta}T_{\gamma\delta} \times\int_0^\infty \left[(\tilde{G}_{1_{\alpha\gamma}})^+_{m_1n_1}(iu)(\tilde{G}_{2_{\beta\delta}})^+_{m_2n_2}(iu) -(\tilde{G}_{1_{\alpha\gamma}})^-_{m_1n_1}(iu)(\tilde{G}_{2_{\beta\delta}})^-_{m_2n_2}(iu)\right] du \quad (4.10)$$

where analogously to (4.8) we have introduced dynamic transition **G** tensors [1]

$$(\tilde{G}_{\alpha\beta})^+_{mn}(\omega) = \frac{1}{\hbar}\sum_{j\neq n,m}\frac{\omega_{jn}}{\omega_{jn}^2-\omega^2} \times(\langle m\mid\mu_\alpha\mid j\rangle\langle j\mid m_\beta\mid n\rangle+\langle m\mid m_\beta\mid j\rangle\langle j\mid\mu_\alpha\mid n\rangle) \quad (4.11a)$$

$$(\tilde{G}_{\alpha\beta})^-_{mn}(\omega) = \frac{1}{\hbar}\sum_{j\neq n,m}\frac{\omega}{\omega_{jn}^2-\omega^2} \times(\langle m\mid\mu_\alpha\mid j\rangle\langle j\mid m_\beta\mid n\rangle-\langle m\mid m_\beta\mid j\rangle\langle j\mid\mu_\alpha\mid n\rangle) \quad (4.11b)$$

4.2.4 Time reversal characteristics of matrix elements

Our stated aim was to allow for time-odd tensorial parts in the calculation of discriminatory and non-discriminatory dispersion energies. We pause to identify these terms in the results of subsections 4.2.2 and 4.2.3. The dynamic transition tensors in (4.7) and (4.10) which describe the near-zone have corresponding effective operators (1.8) with $\overline{E} = E_n = E_m$ in (1.8j). The behaviour under time reversal of the operators generating these dynamic transition tensors has been discussed in subsection 1.2.1. By time-even and time-odd tensorial parts, in what follows, we mean those parts which are generated by time-even and time-odd operators respectively. It is necessary to note explicitly that we are linking the time-even or time-odd character of a transition tensor with the behaviour of the generating operator, because the behaviour of the associated matrix element with respect to time-reversal is only that of the operator for diagonal transitions. The discriminatory and non-discriminatory interactions in the near-zone limit described by (4.7)

and (4.10) are thus seen to contain contributions from both time-even and time-odd tensors.

4.2.5 Molecules in non-degenerate states

Our results may be shown to be consistent with conventional treatments of systems lacking degeneracy by letting $|m_1\rangle = |n_1\rangle$ and $|m_2\rangle = |n_2\rangle$.

Then, from (4.8), (4.11) and (1.4) it is possible to see that

$$(\tilde{\alpha}_{\alpha\beta})^{+}_{nn}(\omega) = \alpha_{\alpha\beta}(\omega) \tag{4.12a}$$

$$(\tilde{\alpha}_{\alpha\beta})^{-}_{nn}(\omega) = -i\alpha'_{\alpha\beta}(\omega) \tag{4.12b}$$

$$(\tilde{G}_{\alpha\beta})^{+}_{nn}(\omega) = G_{\alpha\beta}(\omega) \tag{4.12c}$$

$$(\tilde{G}_{\alpha\beta})^{-}_{nn}(\omega) = -iG'_{\alpha\beta}(\omega) \tag{4.12d}$$

so that we may write

$$E = -\frac{\hbar}{32\pi^3\epsilon_0^2}T_{\alpha\beta}T_{\gamma\delta} \times \int_0^\infty [\alpha_{1_{\alpha\gamma}}(iu)\alpha_{2_{\beta\delta}}(iu) + \alpha'_{1_{\alpha\gamma}}(iu)\alpha'_{2_{\beta\delta}}(iu)]du \tag{4.13}$$

$$E' = -\frac{\mu_o\hbar}{16\pi^3\epsilon_o}T_{\alpha\beta}T_{\gamma\delta} \times \int_0^\infty [G_{1_{\alpha\gamma}}(iu)G_{2_{\beta\delta}}(iu) + G'_{1_{\alpha\gamma}}(iu)G'_{2_{\beta\gamma}}(iu)]du \tag{4.14}$$

It is usual to discard the terms in the imaginary parts of the polarizability tensors and in the real parts of the **G** tensors, since for an even-electron system it is always possible to choose wavefunctions which are of definite time-reversal symmetry and therefore do not support such time-odd tensor operators [1,14].

If time-even contributions only are retained, it is possible to recover expressions for the discriminatory and non-discriminatory dispersion energies as most commonly found in the literature:

$$E = -\frac{\hbar}{32\pi^3\epsilon_o^2}T_{\alpha\beta}T_{\gamma\delta}$$

$$\times \int_0^\infty \alpha_{1_{\alpha\gamma}}(iu)\alpha_{2_{\beta\delta}}(iu)du \tag{4.15}$$

$$E' = -\frac{\mu_o\hbar}{16\pi^3\epsilon_o}T_{\alpha\beta}T_{\gamma\delta} \times \int_0^\infty G'_{1_{\alpha\gamma}}(iu)G'_{2_{\beta\delta}}(iu)du \tag{4.16}$$

Equation (4.15) is just the well-known London formula for the dispersion energy [62], while equation (4.16) is the fixed orientation form of the result first obtained by Mavroyannis and Stephen for the near-zone limit discriminatory dispersion energy [53].

4.2.6 The dispersion energy of chiral molecules in twofold Kramers degenerate states

Thus far, derived expressions appertain to general degenerate states. Twofold Kramers degeneracy in odd-electron molecules is a simple example which may be considered specifically.

Following the normal convention, the orthogonal spin states for one electron $|\frac{1}{2},\frac{1}{2}\rangle$ and $|\frac{1}{2},-\frac{1}{2}\rangle$ are denoted by α and β respectively. An appropriate choice of basis set for the spin wavefunctions of the two-molecule system would be the following combinations of products of one-electron spin states quantised along the intermolecular axis;

a singlet state

$$|\Sigma^+\rangle = \frac{1}{\sqrt{2}}(|\alpha_1\beta_2\rangle - |\beta_1\alpha_2\rangle) \tag{4.17a}$$

and triplet states

$$|\Pi_{+1}\rangle = |\alpha_1\alpha_2\rangle \tag{4.17b}$$

$$|\Sigma^-\rangle = \frac{1}{\sqrt{2}}(|\alpha_1\beta_2\rangle + |\beta_1\alpha_2\rangle) \tag{4.17c}$$

$$|\Pi_{-1}\rangle = |\beta_1\beta_2\rangle \tag{4.17d}$$

This particular choice ensures that the electric dipole-electric dipole and the magnetic dipole-magnetic dipole perturbation Hamiltonian matrices are immediately in diagonal form since the spin functions (4.17) transform as irreducible representations of the point group to which the molecular pair belongs. The perturbation Hamiltonians span the totally symmetric representation and cannot mix functions spanning different irreducible representations. It follows that these functions are in fact the eigenfunctions of the perturbation Hamiltonians (4.2) and (4.3) [60].

The dispersion energy of molecules encountering in these states is

$$E(\Pi_{\pm 1}) = E_{\alpha_1\alpha_2,\alpha_1\alpha_2} \tag{4.18a}$$

$$E(\Sigma^{\mp}) = E_{\alpha_1\beta_2,\alpha_1\beta_2} \pm E_{\alpha_1\beta_2,\beta_1\alpha_2} \tag{4.18b}$$

where $E_{\alpha_1\alpha_2,\alpha_1\alpha_2}$, $E_{\alpha_1\beta_2,\alpha_1\beta_2}$ and $E_{\alpha_1\beta_2,\beta_1\alpha_2}$ are given by (4.7).

For molecules which are, in addition, chiral it is possible to write analogous results for the discriminatory part of the dispersion interaction:

$$E'(\Pi_{\pm 1}) = E'_{\alpha_1\alpha_2,\alpha_1\alpha_2} \tag{4.19a}$$

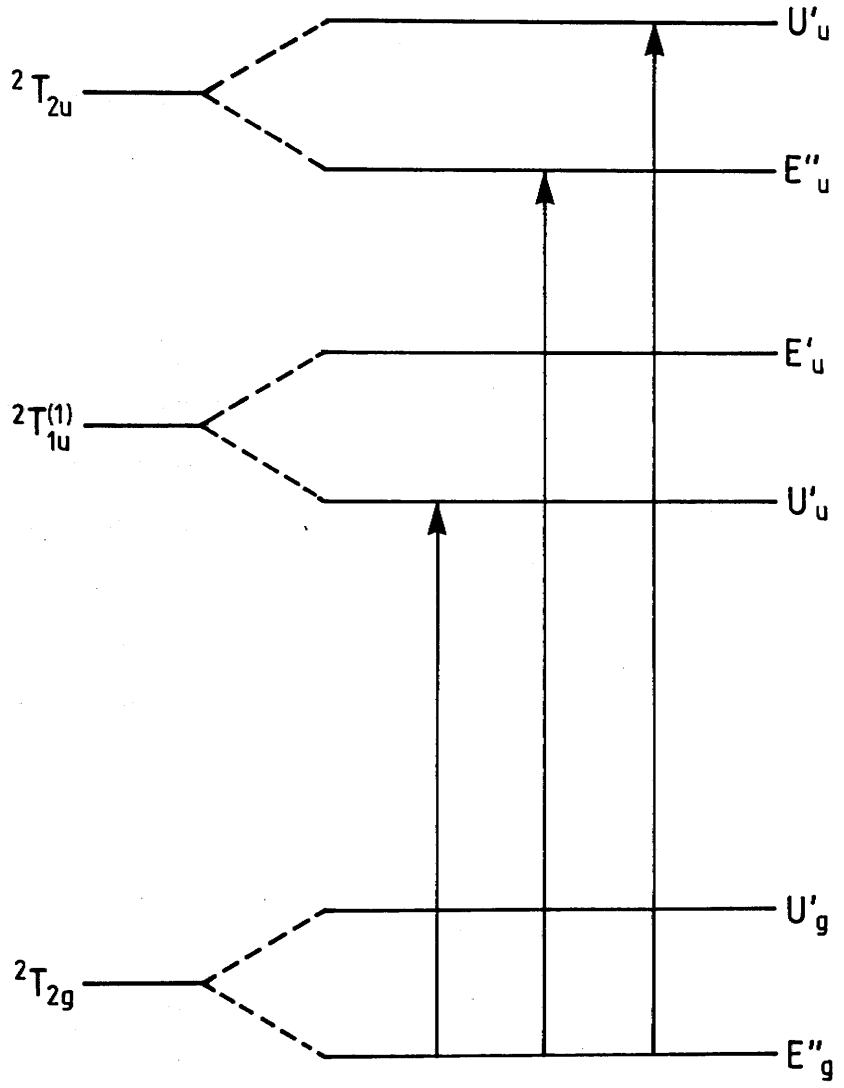
$$E'(\Sigma^{\mp}) = E'_{\alpha_1\beta_2,\alpha_1\beta_2} \pm E'_{\alpha_1\beta_2,\beta_1\alpha_2} \tag{4.19b}$$

where $E'_{\alpha_1\alpha_2,\alpha_1\alpha_2}$, $E'_{\alpha_1\beta_2,\alpha_1\beta_2}$ and $E'_{\alpha_1\beta_2,\beta_1\alpha_2}$ are given by (4.10).

These results for twofold Kramers degeneracy may be put to use in a model calculation on a specific odd-electron chiral molecule. For simplicity a hypothetical transition metal complex of chiral symmetry O^* is chosen. It has already been shown that the large spin-orbit coupling in the charge-transfer states of iridium(IV) hexahalide complexes leads to such molecules being favourable candidates for the study of antisymmetric scattering in the resonance Raman effect [15,18]. The intensity of this scattering is a function of the time-odd part of the transition polarizability $(\tilde{\alpha}_{\alpha\beta})^-_{mn}$ Since the time-odd part of the dispersion interaction is also dependent on $(\tilde{\alpha}_{\alpha\beta})^-_{mn}$, it would seem apposite to endow our hypothetical molecule with the properties of these complexes.

Consequently, the model chiral complex is taken to be low spin d^5 with an energy level pattern identical to that of $IrBr_6^{2-}$ in aqueous solution, as illustrated in fig. 4.1 [63]. The first few electric dipole-allowed transitions, which are in addition $t_g \leftarrow \gamma_u$ charge transfer transitions, are $U_u'(^2T_{1u}^{(1)}) \longleftarrow E_g''(^2T_{2g})$, $E_u''(^2T_{2u}) \longleftarrow E_g''(^2T_{2g})$ and $U_u'(^2T_{2u}) \longleftarrow E_g''(^2T_{2g})$. It is noted that the transition $U_g'(^2T_{2g}) \longleftarrow E_g''(^2T_{2g})$ is electric dipole-forbidden because the initial and final spin-orbit states are derived from the same orbital configuration. Those transitions which are electric dipole-allowed in the parent O_h^* complex are also magnetic dipole-allowed in the molecule of O^* symmetry.

In the calculation of time-even and time-odd contributions to the dispersion energy of alkali metal atoms [60], it was possible to make the assumption that most of the electric dipole oscillator strength originated in $n^2P \leftarrow n^2S$ transitions, rendering tractable the summation over intermediate states required to obtain the polarizability transition tensor components from the dipole matrix elements. The admissibility of such a simplification is atypical. Electronic absorption spectra of iridium hexahalide complexes display a more complicated pattern of bands and it now becomes expedient to take account of excited states which are not necessarily spin-orbit states derived from a common orbital configuration. Bands arising from charge-transfer transitions feature prominently in the spectra. Those corresponding to the transitions illustrated in fig. 4.1 have been assigned using magnetic circular dichroism. They are of the type $t_g \leftarrow \gamma_u$ and characteristically of intermediate intensity. Strong $e_g \leftarrow \gamma_u$ charge transfer bands make a systematic appearance at frequencies higher than those of the $t_g \leftarrow \gamma_u$ transitions [63]. It is obvious that the final states associated with $e_g \leftarrow \gamma_u$ transitions should be included as intermediate levels in our summations because they are of an intensity which more than compensates for their high frequency. However, these bands were not resolved and thus no attempt at assignment was possible. This prohibits rigorous inclusion of these transitions into our calculations.



The first few electric dipole-allowed transitions between the spin-orbit levels of $[IrBr_6]^{2-}$

Fig. 4.1

With these attendant difficulties, a calculation of the relative values of the total time-odd and time-even parts to the discriminatory and non-discriminatory dispersion interaction is not feasible for an O^* molecule modelled on iridium (IV) hexahalide complexes. A less ambitious attempt to calculate the relative magnitudes of time-odd and time-even parts for a specific transition or for transitions with final states of common orbital configuration proves instructive and is in keeping with our desire for a qualitative estimation of magnitudes. Specifically, we shall treat singly the transitions shown in fig. 4.1, combining the results for those transitions with a common orbital configuration.

A direct comparison between time-even and time-odd parts is possible because both can be shown to be a function of the same reduced matrix elements. All possible transition tensor components may be calculated from the Wigner-Eckart theorem for the octahedral double group O^* [1,64] which allows us to write

$$\begin{aligned}\langle \Gamma\gamma|t_X|\Gamma'\gamma'\rangle &= (-1)^{u(\Gamma-\gamma)}\frac{i}{\sqrt{2}}\langle \Gamma \,||\, t \,||\, \Gamma'\rangle \\ &\quad\times\left[\begin{pmatrix}\Gamma & T_1 & \Gamma'\\ -\gamma & 1 & \gamma'\end{pmatrix}-\begin{pmatrix}\Gamma & T_1 & \Gamma'\\ -\gamma & -1 & \gamma'\end{pmatrix}\right] \qquad (4.20a)\\ \langle \Gamma\gamma|t_Y|\Gamma'\gamma'\rangle &= (-1)^{u(\Gamma-\gamma)}\frac{1}{\sqrt{2}}\langle \Gamma \,||\, t \,||\, \Gamma'\rangle \\ &\quad\times\left[\begin{pmatrix}\Gamma & T_1 & \Gamma'\\ -\gamma & 1 & \gamma'\end{pmatrix}+\begin{pmatrix}\Gamma & T_1 & \Gamma'\\ -\gamma & -1 & \gamma'\end{pmatrix}\right] \qquad (4.20b)\\ \langle \Gamma\gamma|t_Z|\Gamma'\gamma'\rangle &= (-1)^{u(\Gamma-\gamma)}(-i)\langle \Gamma \,||\, t \,||\, \Gamma'\rangle\begin{pmatrix}\Gamma & T_1 & \Gamma'\\ -\gamma & 0 & \gamma'\end{pmatrix} \qquad (4.20c)\end{aligned}$$

In this context t_α should be interpreted as either the magnetic or electric dipole moment operator. The states $|\,\Gamma\gamma\rangle$ and $|\,\Gamma'\gamma'\rangle$ are the ground and excited spin orbit states given in fig. 4.1. The function u has been defined, and the possible values it may take listed, by Harnung [64]. Making use of (4.20) and the tables of $3-\Gamma$ symbols given by Harnung we obtain, for example,

$$
\begin{aligned}
&\langle E''(n)\tfrac{1}{2}|\mu_X|E''(j)-\tfrac{1}{2}\rangle \\
\times\langle E''(j)-\tfrac{1}{2}|m_X|E''(n)\tfrac{1}{2}\rangle \;&=\; \frac{1}{2}\langle E''(n)\,||\,\mu\,||\,E''(j)\rangle\langle E''(j)\,||\,m\,||\,E''(n)\rangle \\
&\quad\times\left[\begin{pmatrix} E'' & T_1 & E'' \\ -\frac{1}{2} & 1 & -\frac{1}{2}\end{pmatrix}-\begin{pmatrix} E'' & T_1 & E'' \\ -\frac{1}{2} & -1 & -\frac{1}{2}\end{pmatrix}\right] \\
&\quad\times\left[\begin{pmatrix} E'' & T_1 & E'' \\ \frac{1}{2} & 1 & \frac{1}{2}\end{pmatrix}-\begin{pmatrix} E'' & T_1 & E'' \\ \frac{1}{2} & -1 & \frac{1}{2}\end{pmatrix}\right] \\
&=\; -\frac{1}{6}\langle E''(n)\,||\,\mu\,||\,E''(j)\rangle \\
&\quad\times\langle E''(j)\,||\,m\,||\,E''(n)\rangle
\end{aligned}
\tag{4.21}
$$

All other pertinent matrix elements may be calculated in a similar manner. On making the assumption that the electric and magnetic dipole moment reduced matrix elements are pure real and pure imaginary respectively, the following results are found for the polarizability and optical activity transition tensors:

E'' intermediate level

$(\tilde{\alpha}_{\alpha\beta})^{+}_{mn}$

Common factor $\frac{\omega_{jn}}{\hbar(\omega_{jn}^2-\omega^2)}\,|\langle E''(n)\,||\,\mu\,||\,E''(j)\rangle|^2$

$$
\underset{1/2\leftarrow 1/2}{\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3}\end{pmatrix}}
\underset{-1/2\leftarrow -1/2}{\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3}\end{pmatrix}}
\underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{pmatrix}}
\underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0\end{pmatrix}}
\tag{4.22a}
$$

$(\tilde{\alpha}_{\alpha\beta})^{-}_{mn}$

Common factor $\frac{\omega}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ E''(j)\rangle|^2$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} 0 & \frac{i}{3} & 0 \\ -\frac{i}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} 0 & -\frac{i}{3} & 0 \\ \frac{i}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & \frac{1}{3} \\ 0 & 0 & \frac{i}{3} \\ -\frac{1}{3} & -\frac{i}{3} & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & -\frac{1}{3} \\ 0 & 0 & \frac{i}{3} \\ \frac{1}{3} & -\frac{i}{3} & 0 \end{pmatrix}} \tag{4.22b}$$

$(\tilde{G}_{\alpha\beta})^{+}_{mn}$

Common factor $\frac{\omega_{jn}}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ E''(j)\rangle|\ \ |\langle E''(n)\ ||\ m\ ||\ E''(j)\rangle|$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} 0 & \frac{1}{3} & 0 \\ -\frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} 0 & -\frac{1}{3} & 0 \\ \frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & -\frac{i}{3} \\ 0 & 0 & \frac{1}{3} \\ \frac{i}{3} & -\frac{1}{3} & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & \frac{i}{3} \\ 0 & 0 & \frac{1}{3} \\ -\frac{i}{3} & -\frac{1}{3} & 0 \end{pmatrix}} \tag{4.22c}$$

$(\tilde{G}_{\alpha\beta})^{-}_{mn}$

Common factor $\frac{\omega}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ E''(j)\rangle|\ \ |\langle E''(n)\ ||\ m\ ||\ E''(j)\rangle|$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} -\frac{i}{3} & 0 & 0 \\ 0 & -\frac{i}{3} & 0 \\ 0 & 0 & -\frac{i}{3} \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} -\frac{i}{3} & 0 & 0 \\ 0 & -\frac{i}{3} & 0 \\ 0 & 0 & -\frac{i}{3} \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \tag{4.22d}$$

U' intermediate level

$(\tilde{\alpha}_{\alpha\beta})^{+}_{mn}$

Common factor $\frac{\omega_{jn}}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ U'(j)\rangle|^2$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \tag{4.23a}$$

$(\tilde{\alpha}_{\alpha\beta})^{-}_{mn}$

Common factor $\frac{\omega}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ U'(j)\rangle|^2$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} 0 & -\frac{i}{6} & 0 \\ \frac{i}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} 0 & \frac{i}{6} & 0 \\ -\frac{i}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & -\frac{1}{6} \\ 0 & 0 & -\frac{i}{6} \\ \frac{1}{6} & \frac{i}{6} & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & \frac{1}{6} \\ 0 & 0 & -\frac{i}{6} \\ -\frac{1}{6} & \frac{i}{6} & 0 \end{pmatrix}} \tag{4.23b}$$

$(\tilde{G}_{\alpha\beta})^{+}_{mn}$

Common factor $\frac{\omega_{jn}}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ U'(j)\rangle|\ \ |\langle E''(n)\ ||\ m\ ||\ U'(j)\rangle|$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} 0 & -\frac{1}{6} & 0 \\ \frac{1}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} 0 & \frac{1}{6} & 0 \\ -\frac{1}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & \frac{i}{6} \\ 0 & 0 & -\frac{1}{6} \\ -\frac{i}{6} & \frac{1}{6} & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & -\frac{i}{6} \\ 0 & 0 & -\frac{1}{6} \\ \frac{i}{6} & \frac{1}{6} & 0 \end{pmatrix}} \tag{4.23c}$$

$(\tilde{G}_{\alpha\beta})^{-}_{mn}$

Common factor $\frac{\omega}{\hbar(\omega_{jn}^2-\omega^2)}\ |\langle E''(n)\ ||\ \mu\ ||\ U'(j)\rangle|\ \ |\langle E''(n)\ ||\ m\ ||\ U'(j)\rangle|$

$$\underset{1/2\leftarrow 1/2}{\begin{pmatrix} -\frac{i}{3} & 0 & 0 \\ 0 & -\frac{i}{3} & 0 \\ 0 & 0 & -\frac{i}{3} \end{pmatrix}} \underset{-1/2\leftarrow -1/2}{\begin{pmatrix} -\frac{i}{3} & 0 & 0 \\ 0 & -\frac{i}{3} & 0 \\ 0 & 0 & -\frac{i}{3} \end{pmatrix}} \underset{-1/2\leftarrow 1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \underset{1/2\leftarrow -1/2}{\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}} \tag{4.23d}$$

Having found the contributions from individual transitions of symmetries U' and E'' to the property and transition tensor components associated with the discriminatory and non-discriminatory dispersion interaction, we are now in a position to calculate the contributions to the eigenvalues of the two-molecule system originating in these specified transitions.

We begin by considering the discriminatory dispersion interaction. The property tensors of each molecule are referred to a common axis system X, Y, Z attached to the pair, with Z along the position vector $\mathbf{R}$ which connects the local origins, so that we may write

$$\begin{aligned} T_{\alpha\beta}T_{\gamma\delta}\tilde{G}_{1\alpha\gamma}\tilde{G}_{2\beta\delta} \;=\; & R^{-6}[\tilde{G}_{1XX}\tilde{G}_{2XX} + \tilde{G}_{1YY}\tilde{G}_{2YY} + 4\tilde{G}_{1ZZ}\tilde{G}_{2ZZ} \\ & +\tilde{G}_{1XY}\tilde{G}_{2XY} + \tilde{G}_{1YX}\tilde{G}_{2YX} \\ & -2(\tilde{G}_{1XZ}\tilde{G}_{2XZ} + \tilde{G}_{1ZX}\tilde{G}_{2ZX} \\ & +\tilde{G}_{1YZ}\tilde{G}_{2YZ} + \tilde{G}_{1ZY}\tilde{G}_{2ZY})] \end{aligned} \tag{4.24}$$

To calculate the eigenvalues, we make use of (4.10), inserting the appropriate tensor components of (4.22c), (4.22d), (4.23c) and (4.23d).

Considering an excited level of U' symmetry, we have, for example,

$$\begin{aligned} T_{\alpha\beta}T_{\gamma\delta}\int_0^\infty & [(\tilde{G}_{1\alpha\gamma})^{+}_{+\frac{1}{2}+\frac{1}{2}}(iu) \\ & \times(\tilde{G}_{2\beta\delta})^{+}_{+\frac{1}{2}+\frac{1}{2}}(iu)]du \;=\; \frac{1}{18\hbar^2R^6}\int_0^\infty \frac{\omega_{U'}^2}{(\omega_{U'}^2-\omega^2)^2}du \end{aligned}$$

$$
\begin{aligned}
&\times |\langle E''(^2T_{2g}) \,||\, \mu \,||\, U'(^2T_{1u}^{(1)})\rangle|^2 \\
&\times |\langle E''(^2T_{2g}) \,||\, m \,||\, U'(^2T_{1u}^{(1)})\rangle|^2 \\
= \;& \frac{\pi}{72\hbar^2 R^6 \omega_{U'}} \\
&\times |\langle E''(^2T_{2g}) \,||\, \mu \,||\, U'(^2T_{1u}^{(1)})\rangle|^2 \\
&\times |\langle E''(^2T_{2g}) \,||\, m \,||\, U'(^2T_{1u}^{(1)})\rangle|^2 \qquad (4.25)
\end{aligned}
$$

The time-odd and time-even contributions to $E'_{\alpha_1\alpha_2,\alpha_1\alpha_2}$, $E'_{\alpha_1\beta_2,\alpha_1\beta_2}$ and $E'_{\alpha_1\beta_2,\beta_1\alpha_2}$ associated with excited levels of U' and E'' symmetry are displayed in table 4.1. An obvious adaptation of the noted procedure yields the time-odd and time-even contributions to $E_{\alpha_1\alpha_2,\alpha_1\alpha_2}$, $E_{\alpha_1\beta_2,\alpha_1\beta_2}$ and $E_{\alpha_1\beta_2,\beta_1\alpha_2}$. For completeness, these results are collected in table 4.2. From table 4.1 it may by seen that the discriminatory dispersion energy is given by $E'^q_{E''} = E'_{o_{E''}}(1+\lambda^q)$ and $E'^q_{U'} = E'_{o_{U'}}(1+\frac{\lambda^q}{4})$ where

$$
\begin{aligned}
E'_{0,\mathcal{X}} \;=\; & \frac{\mu_o}{96\hbar\pi^2\epsilon_o R^6 \omega_{,\mathcal{X}}} \\
& \times |\langle E''(n) \,||\, \mu \,||\, \mathcal{X}(j)\rangle|^2 |\langle E''(n) \,||\, m \,||\, \mathcal{X}(j)\rangle|^2 \qquad (4.26)
\end{aligned}
$$

is the conventional discriminatory dispersion energy deriving from time-even tensorial components and associated with excited level $\mathcal{X}$. The conventional discriminatory dispersion energy $E'_{0,\mathcal{X}}$ is augmented by a term originating in time-odd tensorial components and parameterised by λ^q, where λ^q is a characteristic of the eigenstate $|q\rangle$ of the two-molecule system and takes the values $-1, -\frac{1}{3}$ and $\frac{5}{3}$ for the states $|\Sigma^+\rangle$, $|\Pi_{\pm 1}\rangle$ and $|\Sigma^-\rangle$ respectively. Similarly, from table 4.2, it may be seen that the non-discriminatory dispersion energy is given by $E^q_{E''} = E_{o_{E''}}(1+\lambda^q)$ and $E^q_{U'} = E_{o_{U'}}(1+\frac{\lambda^q}{4})$ where

$$
E_{0,\mathcal{X}} = -\frac{1}{192\hbar\pi^2\epsilon_o^2 R^6 \omega_{,\mathcal{X}}} |\langle E''(n) \,||\, \mu \,||\, \mathcal{X}(j)\rangle|^4 \qquad (4.27)
$$

These results show that in the case of the O^* model complex, the conventional spin-independent non-discriminatory dispersion energy is negative, indicative of an attractive interaction whereas the conventional discriminatory dispersion energy is

Table 4.1

Contributions to the discriminatory dispersion interaction.

Excited level	$U'_{\alpha_1\alpha_2,\alpha_1\alpha_2}$		$U'_{\alpha_1\beta_2,\alpha_1\beta_2}$		$U'_{\alpha_1\beta_2,\beta_1\alpha_2}$	
	G^+G^+	G^-G^-	G^+G^+	G^-G^-	G^+G^+	G^-G^-
E'', Common factor: $-\frac{\mu_o}{96\hbar\pi^2\epsilon_o R^6\omega_{E''}}\ \lvert\langle E''(n)\ \|\|\ \mu\ \|\|\ E''(j)\rangle\rvert^2\lvert\langle E''(n)\ \|\|\ m\ \|\|\ E''(j)\rangle\rvert^2$	$\frac{1}{3}$	1	$-\frac{1}{3}$	1	$-\frac{4}{3}$	0
U', Common factor: $-\frac{\mu_o}{96\hbar\pi^2\epsilon_o R^6\omega_{U'}}\ \lvert\langle E''(n)\ \|\|\ \mu\ \|\|\ U'(j)\rangle\rvert^2\lvert\langle E''(n)\ \|\|\ m\ \|\|\ U'(j)\rangle\rvert^2$	$\frac{1}{12}$	1	$-\frac{1}{12}$	1	$-\frac{1}{3}$	0

Table 4.2

Contributions to the non-discriminatory dispersion interaction.

Excited level	$U_{\alpha_1\alpha_2,\alpha_1\alpha_2}$		$U_{\alpha_1\beta_2,\alpha_1\beta_2}$		$U_{\alpha_1\beta_2,\beta_1\alpha_2}$	
	$\alpha^+\alpha^+$	$\alpha^-\alpha^-$	$\alpha^+\alpha^+$	$\alpha^-\alpha^-$	$\alpha^+\alpha^+$	$\alpha^-\alpha^-$
E'', Common factor: $-\frac{1}{192\hbar\pi^2\epsilon_o^2 R^6\omega_{E''}}\ \lvert\langle E''(n)\ \|\|\ \mu\ \|\|\ E''(j)\rangle\rvert^4$	1	$\frac{1}{3}$	1	$-\frac{1}{3}$	0	$-\frac{4}{3}$
U', Common factor: $-\frac{1}{192\hbar\pi^2\epsilon_o^2 R^6\omega_{U'}}\ \lvert\langle E''(n)\ \|\|\ \mu\ \|\|\ U'(j)\rangle\rvert^4$	1	$\frac{1}{12}$	1	$-\frac{1}{12}$	0	$-\frac{1}{3}$

positive for molecules of the same absolute configuration indicative of a repulsive interaction. Molecules belonging to any chiral point group yield these same results for the conventional discriminatory and non-discriminatory dispersion energies upon orientational averaging [52,61]. However, it is not in general possible to predict whether either type of conventional dispersion interaction is attractive or repulsive for a specific intermolecular configuration of two chiral molecules without recourse to detailed calculation.

The combined contribution from the $E_u''(^2T_{2u})$ and $U_u'(^2T_{2u})$ levels to the non-discriminatory dispersion energy may be expressed in terms of one reduced transition matrix element, since [65]

$$|\langle E_g''(^2T_{2g}) \mid\mid \mu \mid\mid E_u''(^2T_{2u})\rangle|^2 = 2\,|\langle E_g''(^2T_{2g}) \mid\mid \mu \mid\mid U_u'(^2T_{2u})\rangle|^2 \tag{4.28}$$

Writing the result explicitly is instructive as this allows an interesting comparison to be made between the O^* complex and the symmetry-related alkali metal atom treated by Buckingham and Joslin [60].

The tensor pattern for a level of E_u'' symmetry in the O^* complex is the same as for the $^2P_{\frac{1}{2}}$ level of the alkali metal atom. A similar correspondence exists between the tensor pattern for a level of U_u' symmetry in the O^* complex and the $^2P_{\frac{3}{2}}$ level of the alkali metal atom [1,60]. However, the relation between components of spin-orbit split levels is not the same in the two cases.

The polarizability tensor components calculated by Buckingham and Joslin lead to the following contributions to the dispersion energy:

$$\begin{aligned} E_q &= -\frac{|\langle 0 \mid\mid \mu \mid\mid 1\rangle|^4}{432\pi^2\epsilon_o^2\hbar R^6}\left[\frac{4\omega_{P_{1/2}}^2+\omega_{P_{3/2}}^2+13\omega_{P_{1/2}}\omega_{P_{3/2}}}{\omega_{P_{1/2}}(\omega_{P_{1/2}}+\omega_{P_{3/2}})\omega_{P_{3/2}}}\right. \\ &\quad \left.+\frac{\lambda^q(\omega_{P_{1/2}}-\omega_{P_{3/2}})^2}{6\omega_{P_{1/2}}(\omega_{P_{1/2}}+\omega_{P_{3/2}})\omega_{P_{1/2}}}\right] \end{aligned} \tag{4.29}$$

while for the O^* complex we may write the following:

$$\begin{aligned} E_q &= -\frac{|\langle E''(^2T_{2g}) \mid\mid \mu \mid\mid E''(^2T_{2u})\rangle|^4}{768\pi^2\epsilon_o^2\hbar R^6} \\ &\quad \times\left[\frac{\omega_{E''}^2+4\omega_{U'}^2+13\omega_{E''}\omega_{U'}}{\omega_{E''}(\omega_{E''}+\omega_{U'})\omega_{U'}}+\frac{\lambda^q(\omega_{E''}^2+16\omega_{U'}^2+\omega_{E''}\omega_{U'})}{12\omega_{E''}(\omega_{E''}+\omega_{U'})\omega_{U'}}\right] \end{aligned} \tag{4.30}$$

Clearly, the time-odd contributions associated with ${}^2P_{\frac{1}{2}}$ and ${}^2P_{\frac{3}{2}}$ levels of the alkali metal atom are such as to effect complete cancellation upon summation if the spin-orbit splitting is zero. It is obvious from (4.30) that this is not the case for the spin-orbit components U_u' and E_u'' deriving from the ${}^2T_{2u}$ excited level of the O^* complex, although partial cancellation does result. Furthermore, the spin-orbit split components of ${}^2T_{1u}^{(1)}$ are of symmetry U_u' and E_u' and since transitions to E_u' are electric dipole-forbidden, only transitions to U_u' contribute to the polarizability tensor components, precluding outright the possibility of any inter-level cancellation.

4.3 Discussion

In collating these results, a crucial point emerges. The complete dependence of the size of a time-odd contribution on the difference in energy of spin-orbit split states is a consequence of the specific polarizability matrix interrelations found for the alkali metal atom. The concomitant limitation of the ratio of the time-odd contribution to the time-even contribution to being at most $\sim 10^{-4}$ is thus not a general characteristic of all systems capable of supporting time-odd tensor components. Indeed, we have shown explicitly that it is not the case for the dispersion energy of O^* complexes. We must, therefore, admit the viability of systems in which the magnitude of the time-odd contribution to the dispersion interaction is comparable to the time-even contribution. This suggests that time-odd contributions may give rise to physically observable effects, and that an experimental investigation of such effects is a realistic proposition. In conjunction, the interesting possibilities arising from consideration of the application of an external magnetic field could be explored. This would enable controlled manipulation of the separation of energy levels, and hence of spin-dependent dispersion interactions.

Chapter 5

Quantum electrodynamic development

5.1 Introduction

In the previous chapter a semi-classical treatment of the discriminatory and non-discriminatory dispersion energy for the near-zone region was detailed. It is also of interest to discuss the wave-zone. In this region, interacting molecules are sufficiently far apart that retardation effects due to the finite speed of light become significant and a full quantum electrodynamic treatment is appropriate. We develop expressions to describe the discriminatory and non-discriminatory dispersion energy at all intermolecular separations outwith the region of electron overlap with the near-zone and wave-zone as limiting cases.

Our calculations follow closely the work of Craig, Power and Thirunamachandran [54,55,58,61]. However, in a generalisation of the specific near-zone results of chapter four, we introduce novel time-odd terms supported by odd-electron molecules and other systems lacking time-reversal invariance [1,60]. No attempt is made at a detailed discussion of quantum electrodynamics, a subject well-served

by text-books [33,61,66]. It suffices to say that therein the electromagnetic field is introduced as a quantised entity. The quantum mechanical molecule and classical radiation field of the semi-classical paradigm become a fully-integrated quantum mechanical system, a complete description of which must include the quantum state of the photon. We employ a semi-colon to separate the specification of molecular and photon states. Within the multipolar formalism, the mediators of intermolecular interactions are virtual photons. In particular, the dispersion interaction is associated with exchange of virtual photons deriving from fluctuations in the quantum vacuum [58,61].

We shall discuss the non-discriminatory and discriminatory parts of the dispersion interaction in subsections 5.2.3 and 5.2.4 respectively.

5.2 Theory

5.2.1 Time-ordered graphs

The starting point in all calculations is the expression from fourth-order perturbation theory for the energy of interaction. Our task is to develop the interaction Hamiltonian matrix elements for each mode of two-photon exchange in order to obtain the associated contribution to the dispersion energy, and then to sum over all possible contributions. Types of two-photon exchange may be illustrated by time-ordered graphs, which provide a helpful pictorial framework on which to base calculation. In time-ordered graphs, virtual photons are delineated by an internal wavy line joining the vertical lines which display the quantum states of the interacting molecules as a function of time. It is a consequence of the virtual character of the processes involved that the photon path is represented by an internal line. Photon pathways appear external to the area between the lines associated with the time progress of each molecule when real absorption or emission occurs. The

vertices of the graphs are labelled by interaction type. Within the dipole approximation, all such vertices in the non-discriminatory dispersion energy calculations are associated with electric dipole interactions, while in the evaluation of the discriminatory dispersion energy, all appropriate combinations of electric and magnetic dipole interactions must be included [61].

5.2.2 A quantum electrodynamic development of the dispersion interaction

The perturbation Hamiltonian for the interaction of molecules 1 and 2 is given by (4.1) with the following expressions for H_E and H_M in the dipole approximation obtained from a quantum electrodynamic treatment:

$$H_E = -\epsilon_0^{-1}\mu_{1_\alpha} d_\alpha^\perp(\mathbf{R}_1) - \epsilon_0^{-1}\mu_{2_\alpha} d_\alpha^\perp(\mathbf{R}_2) \tag{5.1}$$

$$H_M = -m_{1_\alpha} b_\alpha(\mathbf{R}_1) - m_{2_\alpha} b_\alpha(\mathbf{R}_2) \tag{5.2}$$

where μ_α and m_α are given by (1.5a) and (4.4b) respectively, $d_\alpha(\mathbf{R})$ is the microscopic displacement vector, the transverse component of which is indicated by the symbol $\perp$, and $b_\alpha(\mathbf{R})$ is the magnetic field vector. As in chapter four, we find the perturbation Hamiltonian matrix elements for the general case of molecule 1 with degenerate levels $|n_1\rangle$ and $|m_1\rangle$ and molecule 2 with degenerate levels $|n_2\rangle$ and $|m_2\rangle$ from which the eigenvalues for a specific case such as Kramers degeneracy in odd-electron molecules could easily be deduced.

5.2.3 The non-discriminatory dispersion energy

We may write for the dispersion interaction energy between non-polar molecules

1 and 2 [61,p152]

$$E_{m_1m_2,n_1n_2} = -\sum_{I,II,III} \frac{\langle 0' \mid H_{int} \mid III\rangle\langle III \mid H_{int} \mid II\rangle\langle II \mid H_{int} \mid I\rangle\langle I \mid H_{int} \mid 0\rangle}{(E_I - E_0)(E_{II} - E_0)(E_{III} - E_0)} \tag{5.3}$$

where $|0\rangle$ and $|0'\rangle$ are degenerate ground states of the system $|n_1n_2;0\rangle$ and $|m_1m_2;0\rangle$, $|I\rangle$, $|II\rangle$ and $|III\rangle$ are intermediate states and $H_{int} = H_E$ which is given by (5.1). From graph 5.1 we obtain [61,p153]

$$\begin{aligned}\langle I \mid H_{int} \mid 0\rangle &= \langle 1(\mathbf{p}'\lambda'); j_1n_2 \mid -\epsilon_0^{-1}\mu_{1_\alpha} d_\alpha^\perp(\mathbf{R}_1) \mid n_1n_2;0\rangle \\ &= -\epsilon_0^{-1}\langle j_1 \mid \mu_{1_\alpha} \mid n_1\rangle\langle 1(\mathbf{p}'\lambda') \mid d_\alpha^\perp(\mathbf{R}_1) \mid 0\rangle \\ &= i\sum_{\mathbf{p}',\lambda'} \left(\frac{\hbar cp'}{2\epsilon_o V}\right)^{\frac{1}{2}} [f_\alpha^{(\lambda')}(\mathbf{p}')]^*\langle j_1 \mid \mu_\alpha \mid n_1\rangle e^{-i\mathbf{p}'.\mathbf{R}_1}\end{aligned} \tag{5.4}$$

where $f_\alpha^{(\lambda')}(\mathbf{p}')$ is the photon polarization vector associated with polarization λ' and wave vector $\mathbf{p}'$ and V is the volume of the quantisation box. Calculating the remaining matrix elements for graph 5.1 similarly, we find the contribution to the dispersion energy from this interaction mode to be

$$-\sum_{\substack{\mathbf{p},\mathbf{p}'\\ \lambda,\lambda'\\ j_1,j_2}} \frac{\hbar^2c^2pp'}{4\epsilon_0^2V^2} \frac{f_\gamma^{(\lambda)}(\mathbf{p})[f_\alpha^{(\lambda)}(\mathbf{p})]^* f_\delta^{(\lambda')}(\mathbf{p}')[f_\beta^{(\lambda')}(\mathbf{p}')]^* e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}}}{(E_{j_1n_1} + \hbar cp')(E_{j_1n_1} + E_{j_2n_2})(E_{j_2n_2} + \hbar cp)}$$

$$\times\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle \tag{5.5}$$

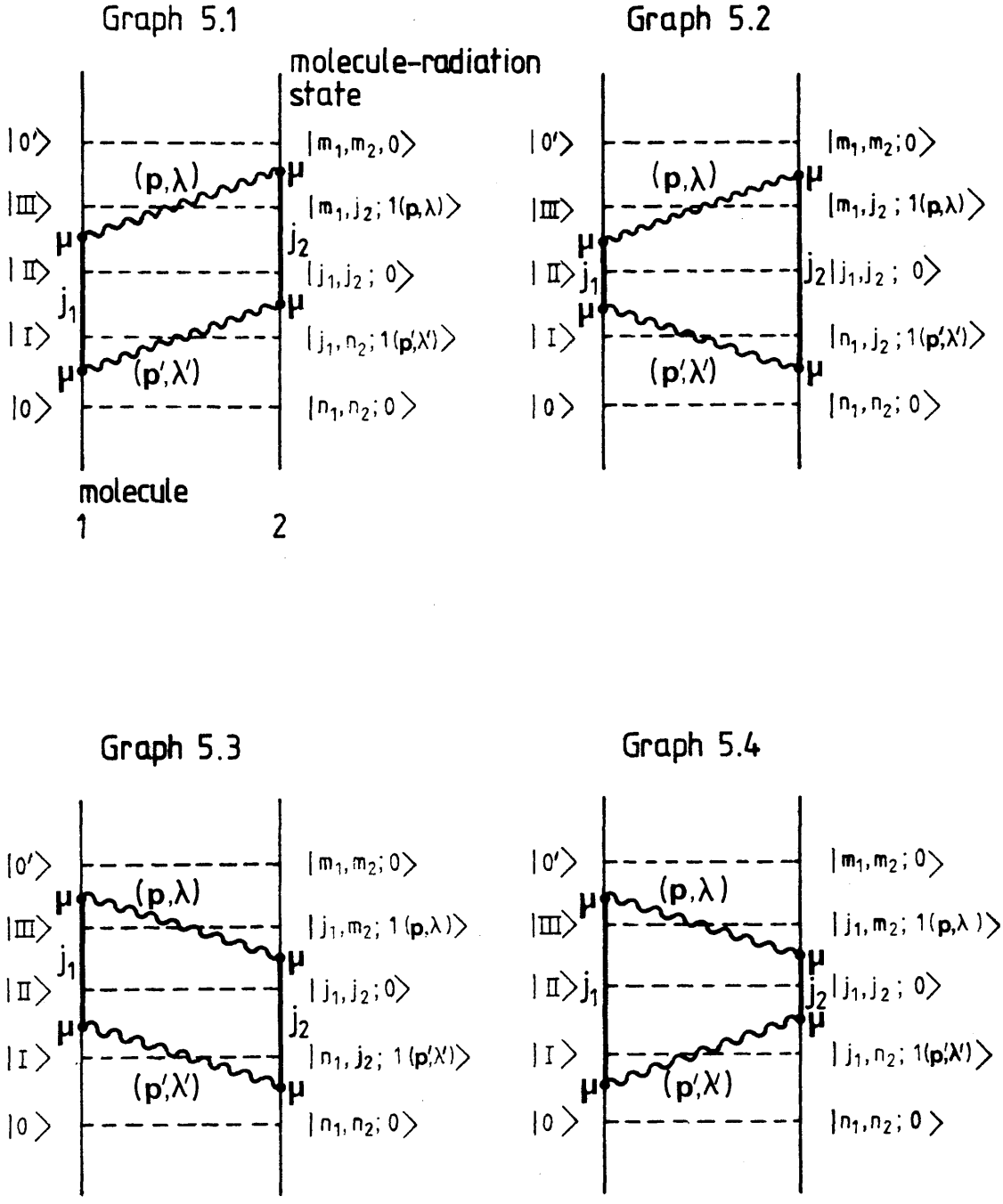
Graphs 5.2-5.12 may then be treated in turn to obtain the contribution to the dispersion energy that each illustrates.

On summation over polarizations λ, λ' using [61,p39]

$$\sum_\lambda f_\alpha^{(\lambda)}(\mathbf{p})[f_\beta^{(\lambda)}(\mathbf{p})]^* = \delta_{\alpha\beta} - \hat{p}_\alpha\hat{p}_\beta \tag{5.6}$$

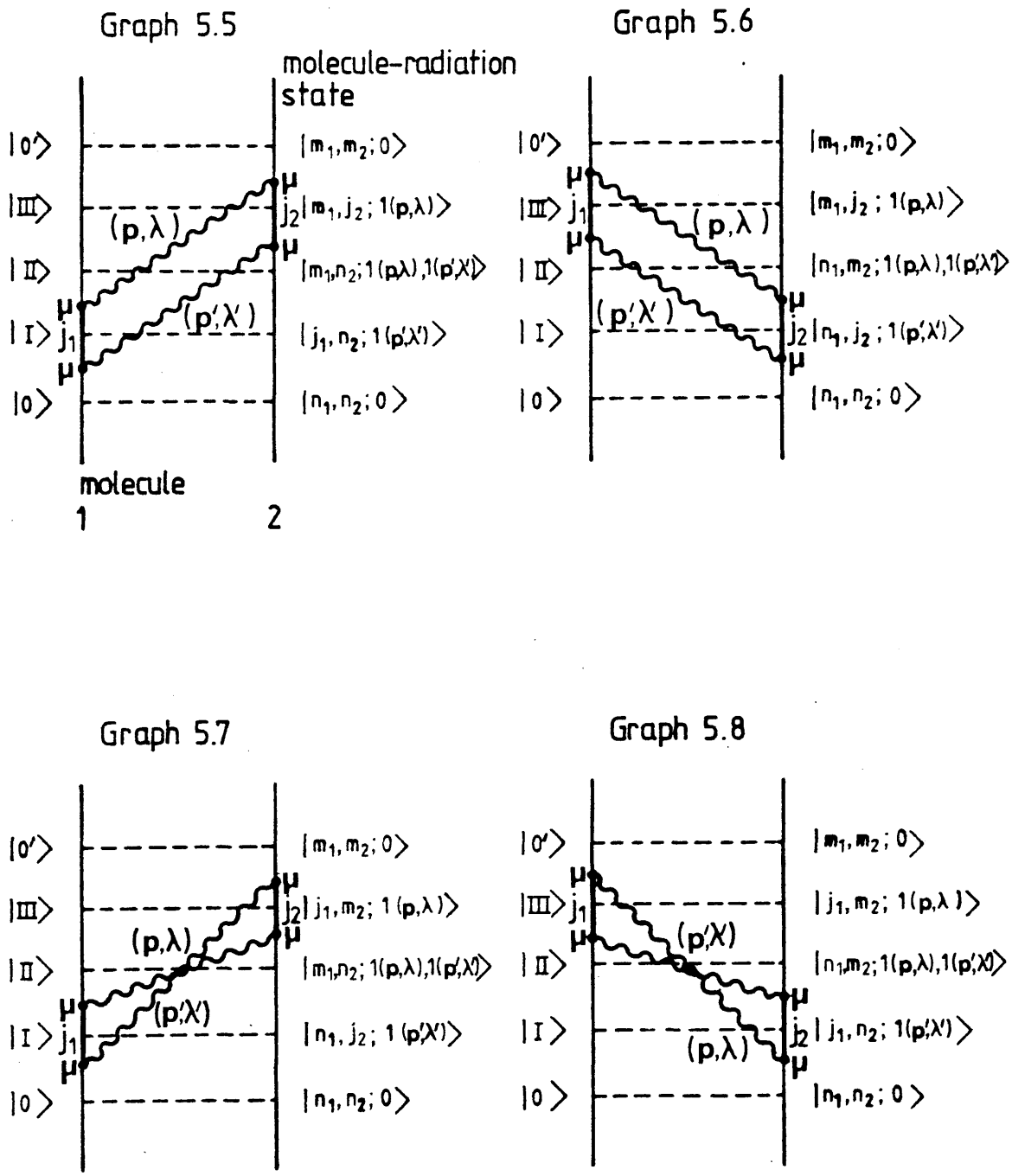
where $\hat{\mathbf{p}}$ is a unit vector along $\mathbf{p}$, we obtain the total dispersion energy

$$\begin{aligned}E_{m_1m_2,n_1n_2} &= -\sum_{\substack{\mathbf{p},\mathbf{p}'\\ j_1,j_2}} \frac{\hbar^2c^2pp'}{4\epsilon_0^2V^2}(\delta_{\alpha\gamma} - \hat{p}_\alpha\hat{p}_\gamma)(\delta_{\beta\delta} - \hat{p}'_\beta\hat{p}'_\delta)e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}} \\ &\quad\times\Big[\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle\end{aligned}$$



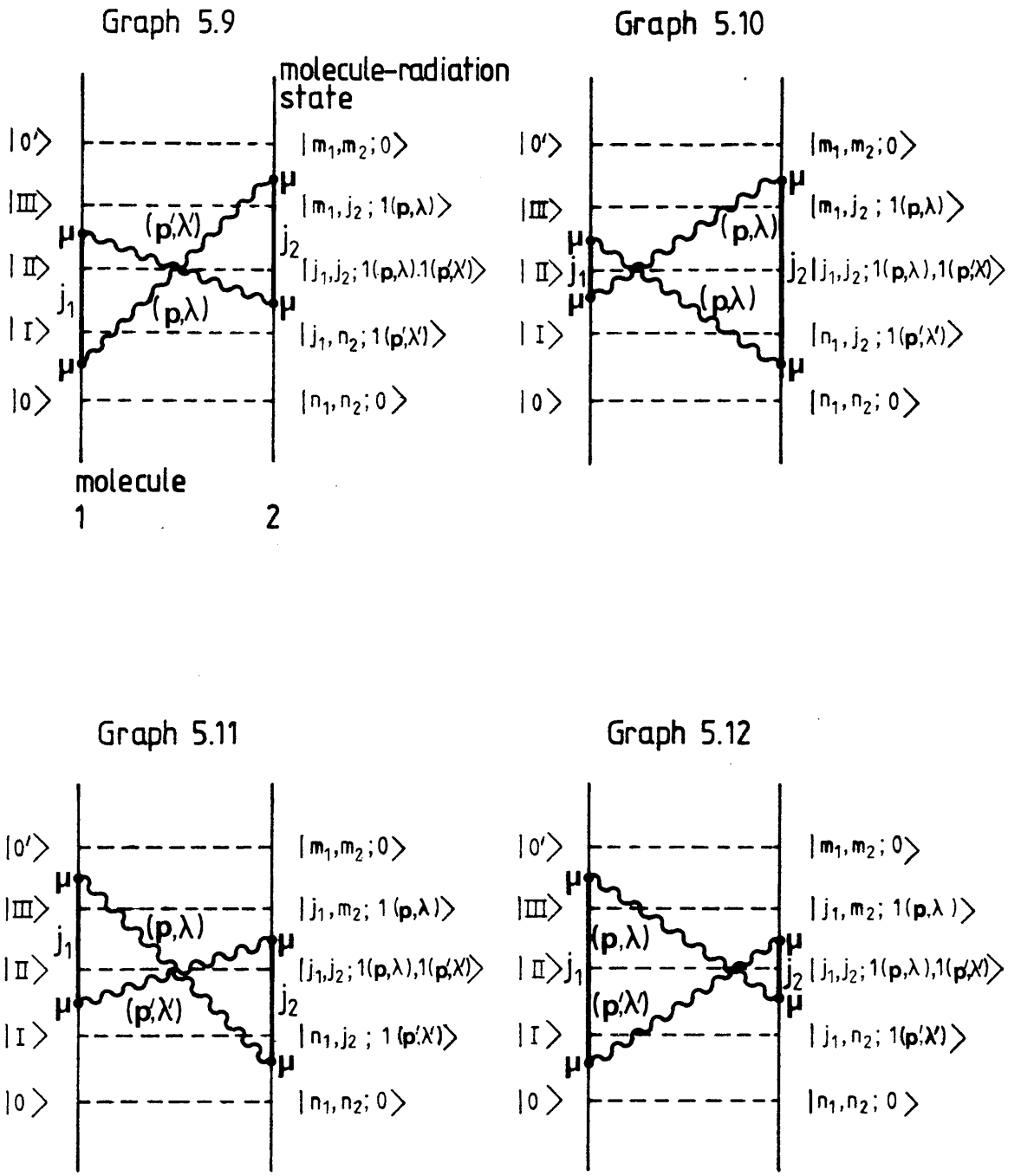
Time-ordered graphs for the non-discriminatory dispersion interaction

Fig. 5.1



Time-ordered graphs for the non-discriminatory dispersion interaction

Fig. 5.2



Time-ordered graphs for the non-discriminatory dispersion interaction

Fig. 5.3

$$
\begin{aligned}
&\times\left(\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}\right.\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp)}\\
&\left.+\frac{1}{(E_{j_2n_2}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\right)\\
&+\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle\\
&\times\left(\frac{1}{(E_{j_1n_1}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\right.\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\\
&\left.\left.+\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\right)\right]
\end{aligned}
\tag{5.7}
$$

where the energy denominators in the first set of parentheses correspond in the order written to graphs 5.1-5.6 and those in the second set, again in the order written, to graphs 5.7-5.12.

This may be rearranged to give [61,p160]

$$
\begin{aligned}
E_{m_1m_2,n_1n_2} \;=\; &-\sum_{\substack{\mathbf{p},\mathbf{p}'\\ j_1,j_2}}\frac{\hbar cpp'(\delta_{\alpha\gamma}-\hat{p}_\alpha\hat{p}_\gamma)(\delta_{\beta\delta}-\hat{p}'_\beta\hat{p}'_\delta)e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}}}{4\epsilon_0^2V^2(E_{j_1n_1}+\hbar cp)(E_{j_2n_2}+\hbar cp)}\\
&\times\left(\frac{1}{p+p'}-\frac{1}{p-p'}\right)\left[\left(\frac{E_{j_1n_1}+E_{j_2n_2}+2\hbar cp}{E_{j_1n_1}+E_{j_2n_2}}\right)\right.\\
&\times(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid\mu_\delta\mid n_2\rangle\\
&\left.+\langle m_1\mid\mu_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)\right.
\end{aligned}
$$

$$+(\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle$$
$$+\langle m_1 \mid \mu_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle)\Big] \quad (5.8)$$

We replace summation over $\mathbf{p}$, $\mathbf{p}'$ by integration using [61,p147]

$$\frac{1}{V}\sum_{\mathbf{p}} \overset{V\to\infty}{\Longrightarrow} \int \frac{d^3\mathbf{p}}{(2\pi)^3} \quad (5.9)$$

and

$$d^3\mathbf{p} = p^2\, dp\, d\Omega \quad (5.10)$$

where $d\Omega$ is an element of solid angle. Angular integration is effected using [61,p148]

$$\begin{aligned}\int(\delta_{\alpha\beta} - \hat{p}_\alpha\hat{p}_\beta)e^{\pm i\mathbf{p}.\mathbf{R}}d\Omega &= 4\pi\left[S_{\alpha\beta}\frac{\sin pR}{p} - RT_{\alpha\beta}\left(\frac{\cos pR}{p^2} - \frac{\sin pR}{p^3R}\right)\right] \\ &= 4\pi\mathcal{T}_{\alpha\beta}(pR) \end{aligned} \quad (5.11)$$

where $T_{\alpha\beta}$ is defined by (4.4a) and we have introduced the tensor

$$S_{\alpha\beta} = \nabla_\alpha\nabla_\beta R = (R^2\delta_{\alpha\beta} - R_\alpha R_\beta)R^{-3} \quad (5.12)$$

Thus

$$\begin{aligned}E_{m_1m_2,n_1n_2} = &-\frac{\hbar c}{16\epsilon_o^2\pi^4}\int_0^\infty\int_0^\infty \sum_{j_1,j_2}\left\{\frac{\mathcal{T}_{\alpha\gamma}(pR)\mathcal{T}_{\beta\delta}(p'R)p^3p'^3}{(E_{j_1n_1}+\hbar cp)(E_{j_2n_2}+\hbar cp)}\right. \\ &\times\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)\left[\left(\frac{E_{j_1n_1}+E_{j_2n_2}+2\hbar cp}{E_{j_1n_1}+E_{j_2n_2}}\right)\right. \\ &\times(\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle \\ &+\langle m_1 \mid \mu_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle\langle m_2 \mid \mu_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle) \\ &+(\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle \\ &+\langle m_1 \mid \mu_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle \\ &\left.\left.\times\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle)\right]\right\}dp\, dp' \end{aligned} \quad (5.13)$$

The integrand is even in p' and we may therefore write [61,p162]

$$\int_0^\infty \mathcal{T}_{\beta\delta}(p'R)\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)p'^3dp' =$$
$$\frac{1}{2}\int_{-\infty}^\infty \mathcal{T}_{\beta\delta}(p'R)\left(\frac{1}{p+p'} - \frac{1}{p-p'}\right)p'^3dp'$$

$$= \pi p^3 \left[S_{\beta\delta} \frac{\cos pR}{p} + RT_{\beta\delta} \left(\frac{\sin pR}{p^2} + \frac{\cos pR}{p^3 R} \right) \right]$$
$$= \pi p^3 \mathcal{T}'_{\beta\delta}(pR) \tag{5.14}$$

where we have used the residue theorem on appropriately chosen contours, with poles at $p' = \pm p$. $\mathcal{T}'_{\alpha\beta}(pR)$ and $\mathcal{T}_{\alpha\beta}(pR)$ are respectively the real and imaginary parts of [61,p162]

$$F_{\alpha\beta}(pR) = \left\{ \frac{S_{\alpha\beta}}{p} - RT_{\alpha\beta} \left(\frac{i}{p^2} - \frac{1}{p^3 R} \right) \right\} e^{ipR} \tag{5.15}$$

Therefore we may write (5.13) as

$$\begin{aligned} E_{m_1 m_2, n_1 n_2} = & \frac{-\hbar c}{16\pi^3 \epsilon_o^2} \\ & \times \int_0^\infty \sum_{j_1, j_2} \left\{ \frac{\left[\mathrm{Re}[F_{\alpha\gamma}(pR)] \mathrm{Im}[F_{\beta\delta}(pR)] + \mathrm{Im}[F_{\alpha\gamma}(pR)] \mathrm{Re}[F_{\beta\delta}(pR)] \right] p^6}{(E_{j_1 n_1} + \hbar cp)(E_{j_2 n_2} + \hbar cp)} \right. \\ & \times \left[\left(\frac{E_{j_1 n_1} + E_{j_2 n_2} + 2\hbar cp}{E_{j_1 n_1} + E_{j_2 n_2}} \right) \right. \\ & \times \langle m_1 \mid \mu_\alpha \mid j_1 \rangle \langle j_1 \mid \mu_\beta \mid n_1 \rangle \langle m_2 \mid \mu_\gamma \mid j_2 \rangle \langle j_2 \mid \mu_\delta \mid n_2 \rangle \\ & \left. \left. + \langle m_1 \mid \mu_\alpha \mid j_1 \rangle \langle j_1 \mid \mu_\beta \mid n_1 \rangle \langle m_2 \mid \mu_\delta \mid j_2 \rangle \langle j_2 \mid \mu_\gamma \mid n_2 \rangle \right] \right\} dp \end{aligned} \tag{5.16}$$

But

$$\begin{aligned} & \mathrm{Re}[F_{\alpha\gamma}(pR)] \mathrm{Im}[F_{\beta\delta}(pR)] + \mathrm{Im}[F_{\alpha\gamma}(pR)] \mathrm{Re}[F_{\beta\delta}(pR)] \\ & = \frac{1}{2i} \left[F_{\alpha\gamma}(pR) F_{\beta\delta}(pR) - [F_{\alpha\gamma}(pR)]^* [F_{\beta\delta}(pR)]^* \right] \end{aligned} \tag{5.17}$$

Thus substituting (5.15) into (5.16) using (5.17) we obtain

$$\begin{aligned} E_{m_1 m_2, n_1 n_2} = & -\frac{\hbar c}{32\pi^3 \epsilon_o^2 i} \int_0^\infty \sum_{j_1, j_2} \left\{ \frac{p^6}{(E_{j_1 n_1} + \hbar cp)(E_{j_2 n_2} + \hbar cp)} \right. \\ & \times \left[\left\{ S_{\alpha\gamma} S_{\beta\delta} \left(\frac{1}{p^2} \right) - R(S_{\alpha\gamma} T_{\beta\delta} + T_{\alpha\gamma} S_{\beta\delta}) \left(\frac{i}{p^3} - \frac{1}{p^4 R} \right) \right. \right. \\ & \left. + R^2 T_{\alpha\gamma} T_{\beta\delta} \left(-\frac{1}{p^4} - \frac{2i}{p^5 R} + \frac{1}{p^6 R^2} \right) \right\} e^{2ipR} \\ & - \left\{ S_{\alpha\gamma} S_{\beta\delta} \left(\frac{1}{p^2} \right) - R(S_{\alpha\gamma} T_{\beta\delta} + T_{\alpha\gamma} S_{\beta\delta}) \left(-\frac{i}{p^3} - \frac{1}{p^4 R} \right) \right. \end{aligned}$$

$$+R^2 T_{\alpha\gamma} T_{\beta\delta} \left(-\frac{1}{p^4} + \frac{2i}{p^5 R} + \frac{1}{p^6 R^2} \right) \Bigg\} e^{-2ipR} \Bigg]$$
$$\times \Bigg[\left(\frac{E_{j_1 n_1} + E_{j_2 n_2} + 2\hbar c p}{E_{j_1 n_1} + E_{j_2 n_2}} \right)$$
$$\times \langle m_1 \mid \mu_\alpha \mid j_1 \rangle \langle j_1 \mid \mu_\beta \mid n_1 \rangle \langle m_2 \mid \mu_\gamma \mid j_2 \rangle \langle j_2 \mid \mu_\delta \mid n_2 \rangle$$
$$+ \langle m_1 \mid \mu_\alpha \mid j_1 \rangle \langle j_1 \mid \mu_\beta \mid n_1 \rangle$$
$$\times \langle m_2 \mid \mu_\delta \mid j_2 \rangle \langle j_2 \mid \mu_\gamma \mid n_2 \rangle \Bigg] \Bigg\} dp \tag{5.18}$$

This integral may be split into two parts. The first integral contains e^{2ipR} in the integrand, while the second contains e^{-2ipR}. We let $p = iu$ in the first integral and $p = -iu$ in the second integral to give

$$E_{m_1 m_2, n_1 n_2} = \frac{-1}{32\pi^3 \epsilon_o^2 \hbar c} \int_0^\infty \sum_{j_1, j_2} \Bigg\{ \frac{u^4 e^{-2uR}}{(k_{j_1 n_1}^2 + u^2)(k_{j_2 n_2}^2 + u^2)}$$
$$\times \Bigg[S_{\alpha\gamma} S_{\beta\delta} - 2R S_{\alpha\gamma} T_{\beta\delta} \left(\frac{1}{u} + \frac{1}{u^2 R} \right)$$
$$+ R^2 T_{\alpha\gamma} T_{\beta\delta} \left(\frac{1}{u^2} + \frac{2}{u^3 R} + \frac{1}{u^4 R^2} \right) \Bigg]$$
$$\times \Bigg[k_{j_1 n_1} k_{j_2 n_2} (\langle m_1 \mid \mu_\alpha \mid j_1 \rangle \langle j_1 \mid \mu_\beta \mid n_1 \rangle + \langle m_1 \mid \mu_\beta \mid j_1 \rangle \langle j_1 \mid \mu_\alpha \mid n_1 \rangle)$$
$$\times (\langle m_2 \mid \mu_\gamma \mid j_2 \rangle \langle j_2 \mid \mu_\delta \mid n_2 \rangle + \langle m_2 \mid \mu_\delta \mid j_2 \rangle \langle j_2 \mid \mu_\gamma \mid n_2 \rangle)$$
$$+ u^2 (\langle m_1 \mid \mu_\alpha \mid j_1 \rangle \langle j_1 \mid \mu_\beta \mid n_1 \rangle - \langle m_1 \mid \mu_\beta \mid j_1 \rangle \langle j_1 \mid \mu_\alpha \mid n_1 \rangle)$$
$$\times (\langle m_2 \mid \mu_\gamma \mid j_2 \rangle \langle j_2 \mid \mu_\delta \mid n_2 \rangle - \langle m_2 \mid \mu_\delta \mid j_2 \rangle \langle j_2 \mid \mu_\gamma \mid n_2 \rangle) \Bigg] \Bigg\} du \tag{5.19}$$

where $k_{jn} = E_{jn}/\hbar c$.

The complete potential is described by (5.19). It is possible to obtain simpler expressions for the near-zone and wave-zone limiting cases by making use of physical arguments to approximate this general equation. We can expand (5.19) in a Taylor series either in powers of $k_{jn}R$ or $1/(k_{jn}R)$. The former is a suitable choice for $k_{jn}R \ll 1$, that is, the near-zone region (assuming low-lying states to make the more significant contributions), while the latter is suitable for $k_{jn}R \gg 1$, that is, the wave-zone region.

Thus for the wave-zone region, retaining the first term of an expansion in

$1/(k_{jn}R)$, we have

$$
\begin{aligned}
E^{wave\text{-}zone}_{m_1m_2,n_1n_2} &= -\frac{\hbar c}{32\pi^3\epsilon_o^2}\int_0^\infty u^4 e^{-2uR} \\
&\times\left[S_{\alpha\gamma}S_{\beta\delta} - 2RS_{\alpha\gamma}T_{\beta\delta}\left(\frac{1}{u}+\frac{1}{u^2R}\right)\right. \\
&\left.+R^2T_{\alpha\gamma}T_{\beta\delta}\left(\frac{1}{u^2}+\frac{2}{u^3R}+\frac{1}{u^4R^2}\right)\right]du \\
&\times\sum_{j_1,j_2}\frac{1}{E_{j_1n_1}E_{j_2n_2}} \\
&\times\Big[(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle+\langle m_1\mid\mu_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle) \\
&\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid\mu_\delta\mid n_2\rangle+\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)\Big] \qquad (5.20)
\end{aligned}
$$

On completion of the integration we obtain finally

$$
\begin{aligned}
E^{wave\text{-}zone}_{m_1m_2,n_1n_2} &= -\frac{\hbar c}{256\pi^3\epsilon_o^2R^5}[6S_{\alpha\gamma}S_{\beta\delta}-10R^2S_{\alpha\gamma}T_{\beta\delta}+10R^4T_{\alpha\gamma}T_{\beta\delta}] \\
&\times(\tilde{\alpha}_{1_{\alpha\beta}})^{+SL}_{m_1n_1}(\tilde{\alpha}_{2_{\gamma\delta}})^{+SL}_{m_2n_2} \qquad (5.21)
\end{aligned}
$$

where

$$
(\tilde{\alpha}_{\alpha\beta})^{+SL}_{mn} = \lim_{\omega\to0}(\tilde{\alpha}_{\alpha\beta})^{+}_{mn}(\omega) = \sum_j\frac{(\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle+\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle)}{E_{jn}} \qquad (5.22)
$$

The superscript SL indicates the static limit ($\omega\to0$) of the tensor. In the near-zone, again considering only the first term in the expansion in $k_{jn}R$, we may write

$$
\begin{aligned}
E^{near\text{-}zone}_{m_1m_2,n_1n_2} &= -\frac{T_{\alpha\gamma}T_{\beta\delta}}{32\pi^3\epsilon_o^2\hbar c}\int_0^\infty\sum_{j_1,j_2}\left\{\frac{1}{(k^2_{j_1n_1}+u^2)(k^2_{j_2n_2}+u^2)}\right. \\
&\times\Big[k_{j_1n_1}k_{j_2n_2} \\
&\times(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle+\langle m_1\mid\mu_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle) \\
&\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid\mu_\delta\mid n_2\rangle+\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle) \\
&+u^2(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle-\langle m_1\mid\mu_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle) \\
&\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid\mu_\delta\mid n_2\rangle \\
&\left.-\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)\Big]\right\}du \qquad (5.23)
\end{aligned}
$$

Letting $u = i\omega/c$, it is easily shown that (5.23) gives an identical result to (4.7) for $E^{near\text{-}zone}_{m_1m_2,n_1n_2}$.

5.2.4 The discriminatory dispersion energy

Again we make use of (5.3) for the dispersion energy introducing the full perturbation Hamiltonian in dipole approximation (4.1) with H_E and H_M defined by (5.1) and (5.2). We consider those combinations in (5.3) which give rise to a discriminatory interaction, that is, those which involve one electric dipole and one magnetic dipole interaction for each centre. We have illustrated only the four graphs of this type originating from graph 5.1. Analogous permutations are available for graphs 5.2-5.12, so we could draw a total of forty-eight graphs of the contributions to the discriminatory dispersion energy.

From graph 5.1a we obtain

$$\begin{aligned}\langle I \mid H_{int} \mid 0\rangle &= \langle 1(\mathbf{p}'\lambda'); j_1 n_2 \mid -m_{1_\alpha} b_\alpha(\mathbf{R}_1) \mid n_1 n_2; 0\rangle \\ &= -\langle j_1 \mid m_{1_\alpha} \mid n_1\rangle\langle 1(\mathbf{p}'\lambda') \mid b_\alpha(\mathbf{R}_1) \mid 0\rangle \\ &= i\sum_{\mathbf{p}',\lambda}\left(\frac{\mu_0\hbar cp'}{2V}\right)^{\frac{1}{2}} [b_\alpha^{(\lambda')}(\mathbf{p}')]^*\langle j_1 \mid m_\alpha \mid n_1\rangle e^{-i\mathbf{p}'.\mathbf{R}_1} \qquad (5.24)\end{aligned}$$

The other matrix elements of graph 5.1a may be calculated following (5.4) and (5.24). We thus find the contribution to the discriminatory dispersion energy from graph 5.1a to be [61,p170]

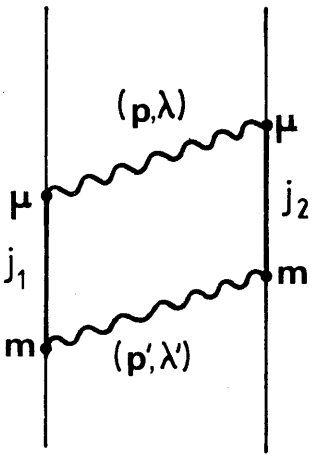
$$-\sum_{\substack{\mathbf{p},\mathbf{p}'\\ \lambda,\lambda'\\ j_1,j_2}} \frac{\mu_o\hbar^2c^2pp'}{4\epsilon_0V^2}\ \frac{f_\gamma^{(\lambda)}(\mathbf{p})[f_\alpha^{(\lambda)}(\mathbf{p})]^* b_\delta^{(\lambda')}(\mathbf{p}')[b_\beta^{(\lambda')}(\mathbf{p}')]^* e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}}}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}$$

$$\times\ \langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid n_2\rangle \qquad (5.25)$$

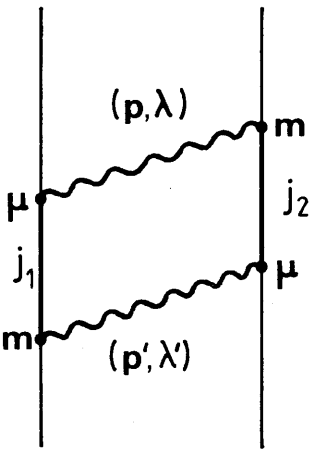
Summing over the forty-eight contributing graphs which are calculated in similar fashion we obtain $E'_{m_1m_2,n_1n_2} = E'_{1\,m_1m_2,n_1n_2} + E'_{2\,m_1m_2,n_1n_2}$ where

$$\begin{aligned}E'_{1\,m_1m_2,n_1n_2} &= -\sum_{\substack{\mathbf{p},\mathbf{p}'\\ j_1,j_2}} \frac{\mu_o\hbar^2c^2pp'}{4\epsilon_0V^2}(\delta_{\alpha\gamma}-\hat{p}_\alpha\hat{p}_\gamma)(\delta_{\beta\delta}-\hat{p}'_\beta\hat{p}'_\delta)e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}} \\ &\quad\times\Big[(\langle n_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid m_1\rangle\langle n_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid m_2\rangle\end{aligned}$$

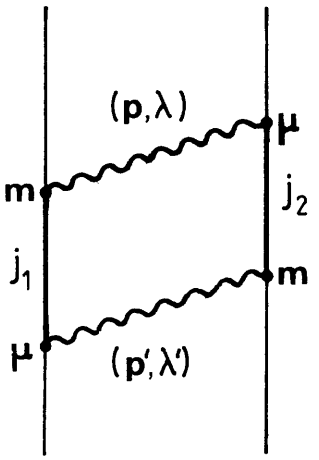
Graph 5.1a



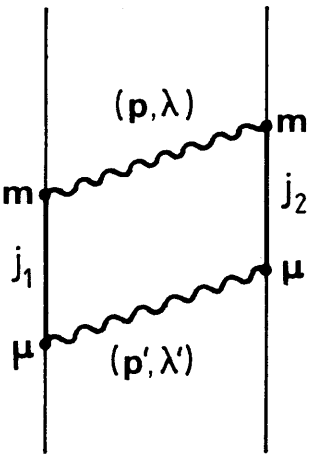
Graph 5.1b



Graph 5.1c



Graph 5.1d



Some time-ordered graphs for the discriminatory dispersion interaction

Fig. 5.4

$$
\begin{aligned}
&+\langle n_1 \mid m_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid m_1\rangle\langle n_2 \mid m_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid m_2\rangle)\\
&\times\Bigg(\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp)}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\Bigg)\\
&+(\langle n_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid m_1\rangle\langle n_2 \mid m_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid m_2\rangle\\
&+\langle n_1 \mid m_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid m_1\rangle\langle n_2 \mid \mu_\delta \mid j_2\rangle\langle j_2 \mid m_\gamma \mid m_2\rangle)\\
&\times\Bigg(\frac{1}{(E_{j_1n_1}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\Bigg)\Bigg]
\end{aligned}
\tag{5.26}
$$

and

$$
\begin{aligned}
E'_{2\,m_1m_2,n_1n_2} \;=\; &-\sum_{\substack{\mathbf{p},\mathbf{p}'\\ j_1,j_2}}\frac{\mu_o\hbar^2c^2pp'}{4\epsilon_0V^2}\epsilon_{\alpha\gamma\mu}\epsilon_{\delta\beta\lambda}\hat{p}_\mu\hat{p}'_\lambda e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}}\\
&\times\Bigg[(\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid n_1\rangle\langle m_2 \mid m_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle\\
&+\langle m_1 \mid m_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid n_2\rangle)\\
&\times\Bigg(\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}
\end{aligned}
$$

$$
\begin{aligned}
&-\frac{1}{(E_{j_2n_2}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_2n_2}+\hbar cp)}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_1n_1}+\hbar cp)}\\
&-\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2})(E_{j_1n_1}+\hbar cp)}\\
&+\frac{1}{(E_{j_1n_1}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp)}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\Bigg)\\
&+(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid m_\gamma\mid n_2\rangle\\
&+\langle m_1\mid m_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)\\
&\times\Bigg(\frac{1}{(E_{j_1n_1}+\hbar cp')(\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&+\frac{1}{(E_{j_2n_2}+\hbar cp)(\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\\
&-\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&-\frac{1}{(E_{j_2n_2}+\hbar cp)(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_2n_2}+\hbar cp')}\\
&-\frac{1}{(E_{j_2n_2}+\hbar cp)(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\\
&-\frac{1}{(E_{j_1n_1}+\hbar cp')(E_{j_1n_1}+E_{j_2n_2}+\hbar cp+\hbar cp')(E_{j_1n_1}+\hbar cp)}\Bigg)\Bigg]
\end{aligned}
\tag{5.27}
$$

where to sum over polarizations λ,λ' we have used (5.6) [61,p39],

$$\sum_\lambda b_\alpha^{(\lambda)}(\mathbf{p})[b_\beta^{(\lambda)}(\mathbf{p})]^* = \delta_{\alpha\beta} - \hat{p}_\alpha\hat{p}_\beta \tag{5.28}$$

and

$$\sum_\lambda f_\alpha^{(\lambda)}(\mathbf{p})[b_\beta^{(\lambda)}(\mathbf{p})]^* = \epsilon_{\alpha\beta\gamma}\hat{p}_\gamma \tag{5.29}$$

Clearly $E'_{1\,m_1m_2,n_1n_2}$ may be developed in a similar way to (5.7) for the non-discriminatory dispersion interaction, so we may immediately write

$$
\begin{aligned}
E'_{1\,m_1m_2,n_1n_2} &= -\frac{\mu_o}{16\epsilon_o\pi^3\hbar c}\int_0^\infty\sum_{j_1,j_2}\Bigg\{\frac{u^4e^{-2uR}}{(k_{j_1n_1}^2+u^2)(k_{j_2n_2}^2+u^2)}\\
&\times\Bigg[S_{\alpha\gamma}S_{\beta\delta}-R(S_{\alpha\gamma}T_{\beta\delta}+T_{\alpha\gamma}S_{\beta\delta})\left(\frac{1}{u}+\frac{1}{u^2R}\right)
\end{aligned}
$$

$$+R^2T_{\alpha\gamma}T_{\beta\delta}\left(\frac{1}{u^2}+\frac{2}{u^3R}+\frac{1}{u^4R^3}\right)\Big]$$
$$\times\Big[k_{j_1n_1}k_{j_2n_2}(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle+\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle)$$
$$\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle+\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)$$
$$+u^2(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle-\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle)$$
$$\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle-\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)\Big]\Big\}du \quad (5.30)$$

It is possible to rearrange (5.27) to give

$$\begin{aligned}
E'_{2\,m_1m_2,n_1n_2} &= -\sum_{\substack{\mathbf{p},\mathbf{p}'\\ j_1,j_2}}\frac{\mu_o\hbar cpp'\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\hat{p}_\mu\hat{p}'_\lambda e^{i(\mathbf{p}+\mathbf{p}').\mathbf{R}}}{4\epsilon_0V^2(E_{j_1n_1}+\hbar cp)(E_{j_2n_2}+\hbar cp)}\left(\frac{1}{p+p'}+\frac{1}{p-p'}\right)\\
&\times\left[\left(\frac{E_{j_1n_1}+E_{j_2n_2}+2\hbar cp}{E_{j_1n_1}+E_{j_2n_2}}\right)\right.\\
&\times\Big[\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle\\
&+\langle m_1\mid m_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid m_\gamma\mid n_2\rangle\\
&+\langle m_1\mid\mu_\beta\mid j_1\rangle\langle j_1\mid m_\alpha\mid n_1\rangle\langle m_2\mid m_\gamma\mid j_2\rangle\langle j_2\mid\mu_\delta\mid n_2\rangle\\
&+\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle\Big]\\
&+\Big[\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle\\
&+\langle m_1\mid m_\alpha\mid j_1\rangle\langle j_1\mid\mu_\beta\mid n_1\rangle\langle m_2\mid m_\gamma\mid j_2\rangle\langle j_2\mid\mu_\delta\mid n_2\rangle\\
&+\langle m_1\mid\mu_\beta\mid j_1\rangle\langle j_1\mid m_\alpha\mid n_1\rangle\langle m_2\mid\mu_\delta\mid j_2\rangle\langle j_2\mid m_\gamma\mid n_2\rangle\\
&\left.+\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle\Big]\right] \quad (5.31)
\end{aligned}$$

Summation over $\mathbf{p}$ and $\mathbf{p}'$ is replaced by integration using (5.9) and (5.10). To perform the angular integration we make use of [61,pp147,148]

$$\begin{aligned}
\int\hat{p}_\alpha e^{\pm i\mathbf{p}.\mathbf{R}}\,d\Omega &= \mp4\pi i\left(\frac{\cos pR}{pR}-\frac{\sin pR}{p^2R^2}\right)\hat{R}_\alpha\\
&= \mp4\pi i\sigma_\alpha(pR) \quad (5.32)
\end{aligned}$$

We therefore find

$$E'_{2\,m_1m_2,n_1n_2} = \frac{\mu_o\hbar c}{16\epsilon_o\pi^4}\int_0^\infty\int_0^\infty\sum_{j_1,j_2}\left\{\frac{\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\sigma_\mu(pR)\sigma_\lambda(p'R)p^3p'^3}{(E_{j_1n_1}+\hbar cp)(E_{j_2n_2}+\hbar cp)}\left(\frac{1}{p+p'}+\frac{1}{p-p'}\right)\right.$$

$$
\begin{aligned}
&\times\left[\left(\frac{E_{j_1 n_1}+E_{j_2 n_2}+2\hbar cp}{E_{j_1 n_1}+E_{j_2 n_2}}\right)\right.\\
&\times[\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid n_1\rangle\langle m_2 \mid m_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle\\
&+\langle m_1 \mid m_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid \mu_\delta \mid j_2\rangle\langle j_2 \mid m_\gamma \mid n_2\rangle\\
&+\langle m_1 \mid \mu_\beta \mid j_1\rangle\langle j_1 \mid m_\alpha \mid n_1\rangle\langle m_2 \mid m_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle\\
&+\langle m_1 \mid m_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid n_2\rangle]\\
&+[\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid n_1\rangle\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid n_2\rangle\\
&+\langle m_1 \mid m_\alpha \mid j_1\rangle\langle j_1 \mid \mu_\beta \mid n_1\rangle\langle m_2 \mid m_\gamma \mid j_2\rangle\langle j_2 \mid \mu_\delta \mid n_2\rangle\\
&+\langle m_1 \mid \mu_\beta \mid j_1\rangle\langle j_1 \mid m_\alpha \mid n_1\rangle\langle m_2 \mid \mu_\delta \mid j_2\rangle\langle j_2 \mid m_\gamma \mid n_2\rangle\\
&\left.+\langle m_1 \mid m_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle\langle m_2 \mid m_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle]\right]\Big\}dpdp'
\end{aligned}
\tag{5.33}
$$

The integrand is even in p' and we find, using the methods of (5.14),

$$
\begin{aligned}
\int_0^\infty \sigma_\lambda(p'R)\left(\frac{1}{p+p'}+\frac{1}{p-p'}\right)p'^3dp' &= \pi p^3\left(\frac{\sin pR}{pR}+\frac{\cos pR}{p^2R^2}\right)\hat{R}_\lambda\\
&= \pi p^3\sigma'_\lambda(pR)
\end{aligned}
\tag{5.34}
$$

It may be seen that $\sigma_\alpha(pR)$ and $\sigma'_\alpha(pR)$ are the real and imaginary parts of

$$
E_\alpha(pR)=\left(\frac{1}{pR}+\frac{i}{p^2R^2}\right)\hat{R}_\alpha e^{ipR} \tag{5.35}
$$

Therefore, following the same procedure as (5.16) to (5.19) in the calculation of the non-discriminatory dispersion energy, we may finally write

$$
\begin{aligned}
E'_{2\,m_1m_2,n_1n_2} = \frac{\mu_o\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\hat{R}_\mu\hat{R}_\lambda}{16\epsilon_o\pi^3R^2\hbar c}\int_0^\infty\sum_{j_1,j_2}\Big\{&\frac{u^4e^{-2uR}}{(k^2_{j_1n_1}+u^2)(k^2_{j_2n_2}+u^2)}\left[1+\frac{2}{uR}+\frac{1}{u^2R^2}\right]\\
&\times[k_{j_1n_1}k_{j_2n_2}(\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid n_1\rangle+\langle m_1 \mid m_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle)\\
&\times(\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid n_2\rangle+\langle m_2 \mid m_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle)\\
&-u^2(\langle m_1 \mid \mu_\alpha \mid j_1\rangle\langle j_1 \mid m_\beta \mid n_1\rangle-\langle m_1 \mid m_\beta \mid j_1\rangle\langle j_1 \mid \mu_\alpha \mid n_1\rangle)\\
&\times(\langle m_2 \mid \mu_\gamma \mid j_2\rangle\langle j_2 \mid m_\delta \mid n_2\rangle-\langle m_2 \mid m_\delta \mid j_2\rangle\langle j_2 \mid \mu_\gamma \mid n_2\rangle)]\Big\}du
\end{aligned}
\tag{5.36}
$$

Adding the expressions given by (5.30) and (5.36) for $E'_{1\,m_1m_2,n_1n_2}$ and $E'_{2\,m_1m_2,n_1n_2}$

we find

$$
\begin{aligned}
E'_{m_1m_2,n_1n_2} &= -\frac{\mu_o}{16\epsilon_o\pi^3\hbar c}\int_0^\infty \sum_{j_1,j_2}\Bigg\{\frac{u^4e^{-2uR}}{(k_{j_1n_1}^2+u^2)(k_{j_2n_2}^2+u^2)} \\
&\times\Bigg[\Bigg[S_{\alpha\gamma}S_{\beta\delta}-R(S_{\alpha\gamma}T_{\beta\delta}+T_{\alpha\gamma}S_{\beta\delta})\left(\frac{1}{u}+\frac{1}{u^2R}\right) \\
&+R^2T_{\alpha\gamma}T_{\beta\delta}\left(\frac{1}{u^2}+\frac{2}{u^3R}+\frac{1}{u^4R^2}\right) \\
&-\frac{\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\hat{R}_\mu\hat{R}_\lambda}{R^2}\left(1+\frac{2}{uR}+\frac{1}{u^2R^2}\right)\Bigg] \\
&\times k_{j_1n_1}k_{j_2n_2}[(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle+\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle) \\
&\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle+\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)] \\
&+\Bigg[S_{\alpha\gamma}S_{\beta\delta}-R(S_{\alpha\gamma}T_{\beta\delta}+T_{\alpha\gamma}S_{\beta\delta})\left(\frac{1}{u}+\frac{1}{u^2R}\right) \\
&+R^2T_{\alpha\gamma}T_{\beta\delta}\left(\frac{1}{u^2}+\frac{2}{u^3R}+\frac{1}{u^4R^2}\right) \\
&+\frac{\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\hat{R}_\mu\hat{R}_\lambda}{R^2}\left(1+\frac{2}{uR}+\frac{1}{u^2R^2}\right)\Bigg] \\
&\times u^2[(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle-\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle) \\
&\times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle-\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle)]\Bigg]\Bigg\}du
\end{aligned}
\tag{5.37}
$$

It is possible to use the arguments put forward in the non-discriminatory case to obtain simpler expressions for the discriminatory interaction in the near-zone and wave-zone limits. We find

$$
\begin{aligned}
E'^{wave\text{-}zone}_{m_1m_2,n_1n_2} &= -\frac{\mu_o\hbar c}{128\epsilon_o\pi^3R^7}[10R^6T_{\alpha\gamma}T_{\beta\delta}-5R^4(T_{\alpha\gamma}S_{\beta\delta}+S_{\alpha\gamma}T_{\beta\delta}) \\
&+6R^2S_{\alpha\gamma}S_{\beta\delta}-14\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\hat{R}_\mu\hat{R}_\lambda](\tilde{G}_{1_{\alpha\beta}})^{+SL}_{m_1n_1}(\tilde{G}_{2_{\gamma\delta}})^{+SL}_{m_2n_2}
\end{aligned}
\tag{5.38}
$$

where

$$
\begin{aligned}
(\tilde{G}_{\alpha\beta})^{+SL}_{mn} &= \lim_{\omega\to0}(\tilde{G}_{\alpha\beta})^{+}_{mn}(\omega) \\
&= \sum_j\frac{(\langle m\mid\mu_\alpha\mid j\rangle\langle j\mid m_\beta\mid n\rangle+\langle m\mid m_\beta\mid j\rangle\langle j\mid\mu_\alpha\mid n\rangle)}{E_{jn}}
\end{aligned}
\tag{5.39}
$$

By including a further term in the expansion in $1/(k_{jn}R)$ we obtain the more rig-

orous result

$$
\begin{aligned}
E^{l\,wave\text{-}zone}_{m_1m_2,n_1n_2} = & -\frac{\mu_o\hbar c}{128\epsilon_o\pi^3R^7}\Big[10R^6T_{\alpha\gamma}T_{\beta\delta}-5R^4(T_{\alpha\gamma}S_{\beta\delta}+S_{\alpha\gamma}T_{\beta\delta}) \\
& +6R^2S_{\alpha\gamma}S_{\beta\delta}-14\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\hat{R}_\mu\hat{R}_\lambda\Big](\tilde{G}_{1_{\alpha\beta}})^{+SL}_{m_1n_1}(\tilde{G}_{2_{\gamma\delta}})^{+SL}_{m_2n_2} \\
& -\frac{\mu_o\hbar^3c^3}{128\epsilon_o\pi^3R^9}\Big[\Big[14R^6T_{\alpha\gamma}T_{\beta\delta}-21R^4(T_{\alpha\gamma}S_{\beta\delta}+S_{\alpha\gamma}T_{\beta\delta}) \\
& +45R^2S_{\alpha\gamma}S_{\beta\delta}-81\epsilon_{\alpha\gamma\mu}\epsilon_{\delta\beta\lambda}\hat{R}_\mu\hat{R}_\lambda\Big] \\
& \times\sum_{j_1,j_2}\left(-\frac{1}{E^3_{j_1n_1}E_{j_2n_2}}-\frac{1}{E_{j_1n_1}E^3_{j_2n_2}}\right) \\
& \times(\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle+\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle) \\
& \times(\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle+\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle) \\
& +\Big[14R^6T_{\alpha\gamma}T_{\beta\delta}-21R^4(T_{\alpha\gamma}S_{\beta\delta}+S_{\alpha\gamma}T_{\beta\delta})+45R^2S_{\alpha\gamma}S_{\beta\delta} \\
& +81\epsilon_{\alpha\gamma\mu}\epsilon_{\delta\beta\lambda}\hat{R}_\mu\hat{R}_\lambda\Big] \\
& \times\sum_{j_1,j_2}\left(\frac{\langle m_1\mid\mu_\alpha\mid j_1\rangle\langle j_1\mid m_\beta\mid n_1\rangle-\langle m_1\mid m_\beta\mid j_1\rangle\langle j_1\mid\mu_\alpha\mid n_1\rangle}{E^2_{j_1n_1}}\right) \\
& \times\left(\frac{\langle m_2\mid\mu_\gamma\mid j_2\rangle\langle j_2\mid m_\delta\mid n_2\rangle-\langle m_2\mid m_\delta\mid j_2\rangle\langle j_2\mid\mu_\gamma\mid n_2\rangle}{E^2_{j_2n_2}}\right)\Big]
\end{aligned}
\tag{5.40}
$$

From the discussion of subsection 1.2.1, (5.38) may be seen to be a function of exclusively time-odd parts and thus may only give a non-zero result for chiral molecules in degenerate states while, as we shall show later, (5.40) is dependent on both time-even and time-odd parts and may be applied to any pair of chiral molecules.

The calculation of $E^{l\,near\text{-}zone}_{m_1m_2,n_1n_2}$ retaining the first term in the expansion in $k_{jn}R$ gives a result identical to (4.10).

5.2.5 Orientational averages

It is possible to perform an average over all orientations of the dispersion energy expressions derived in the preceding two subsections. For the product of the first

rank tensor components P_α and Q_β we have

$$\langle P_\alpha Q_\beta \rangle = \frac{1}{3}\delta_{\alpha\beta} P_\gamma Q_\gamma \tag{5.41}$$

It may also be shown that

$$S_{\alpha\gamma}S_{\beta\delta}\delta_{\alpha\beta}\delta_{\gamma\delta} = \frac{2}{R^2} \tag{5.42a}$$

$$S_{\alpha\gamma}T_{\beta\delta}\delta_{\alpha\beta}\delta_{\gamma\delta} = -\frac{2}{R^4} \tag{5.42b}$$

$$T_{\alpha\gamma}T_{\beta\delta}\delta_{\alpha\beta}\delta_{\gamma\delta} = \frac{6}{R^6} \tag{5.42c}$$

and

$$\epsilon_{\alpha\delta\mu}\epsilon_{\gamma\beta\lambda}\delta_{\alpha\beta}\delta_{\gamma\delta} = -2 \tag{5.43}$$

Making use of (5.41) to (5.43) we obtain the following results:

$$\begin{aligned}\overline{E} = & -\frac{1}{36\pi^3\epsilon_o^2\hbar c R^2}\int_0^\infty \sum_{j_1,j_2}\left\{\frac{u^4 e^{-2uR}}{(k_{j_1n_1}^2+u^2)(k_{j_2n_2}^2+u^2)}\right. \\ & \times\left[1+\frac{2}{uR}+\frac{5}{u^2R^2}+\frac{6}{u^3R^3}+\frac{3}{u^4R^4}\right] \\ & \left.\times k_{j_1n_1}k_{j_2n_2}\,|\langle n_1 \mid \boldsymbol{\mu} \mid j_1\rangle|^2|\langle n_2 \mid \boldsymbol{\mu} \mid j_2\rangle|^2\right\}du\end{aligned} \tag{5.44}$$

$$\overline{E}^{wave\text{-}zone} = \frac{-23\hbar c\alpha_1^{(SL)}\alpha_2^{(SL)}}{64\pi^3\epsilon_o^2 R^7} \tag{5.45}$$

where

$$\alpha^{(SL)} = \frac{2}{3}\sum_j \frac{|\langle n \mid \boldsymbol{\mu} \mid j\rangle|^2}{E_{jn}} \tag{5.46}$$

$$\overline{E}^{near\text{-}zone} = \frac{-3\hbar}{16\pi^3\epsilon_o^2 R^6}\int_0^\infty \alpha_1(iu)\alpha_2(iu)du \tag{5.47}$$

where

$$\alpha(iu) = \frac{2}{3\hbar}\sum_j \frac{\omega_{jn}}{(\omega_{jn}^2-\omega^2)}\,|\langle n \mid \boldsymbol{\mu} \mid j\rangle|^2 \tag{5.48}$$

$$\begin{aligned}\overline{E}' = & -\frac{\mu_o}{18\epsilon_o\pi^3\hbar c R^4}\int_0^\infty \sum_{j_1,j_2}\left\{\frac{u^6 e^{-2uR}}{(k_{j_1n_1}^2+u^2)(k_{j_2n_2}^2+u^2)}\right. \\ & \left.\times\left[\frac{4}{u^2}+\frac{6}{u^3R}+\frac{3}{u^4R^2}\right]\right.\end{aligned}$$

$$\times(\langle n_1 \mid \boldsymbol{\mu} \mid j_1\rangle.\langle j_1 \mid \mathbf{m} \mid n_1\rangle)(\langle n_2 \mid \boldsymbol{\mu} \mid j_2\rangle.\langle j_2 \mid \mathbf{m} \mid n_2\rangle)\Big\}du \tag{5.49}$$

$$\overline{E}^{\prime wave\text{-}zone} = -\frac{\mu_o\hbar^3c^3}{3\epsilon_o\pi^3R^9}\sum_{j_1}\frac{\langle n_1 \mid \boldsymbol{\mu} \mid j_1\rangle.\langle j_1 \mid \mathbf{m} \mid n_1\rangle}{E^2_{j_1n_1}} \times\sum_{j_2}\frac{\langle n_2 \mid \boldsymbol{\mu} \mid j_2\rangle.\langle j_2 \mid \mathbf{m} \mid n_2\rangle}{E^2_{j_2n_2}} \tag{5.50}$$

$$\overline{E}^{\prime near\text{-}zone} = -\frac{3\mu_o\hbar}{8\epsilon_o\pi^3R^6}\int_0^\infty G_1'(iu)G_2'(iu)du \tag{5.51}$$

where

$$G'(iu) = -\frac{2}{3\hbar}\sum_{j\neq n}\frac{\omega}{(\omega^2_{jn}-\omega^2)}\mathrm{Im}(\langle n|\boldsymbol{\mu}|j\rangle.\langle j|\mathbf{m}|n\rangle) \tag{5.52}$$

We note that (5.45) and (5.47) are the familiar Casimir-Polder and London expressions for the spacially averaged non-discriminatory dispersion interaction in the wave-zone and near-zone respectively [61,62,67]. Furthermore, (5.50) and (5.51) are the standard results for the spacially averaged discriminatory dispersion interaction in the wave-zone and near-zone respectively [53,61].

Although these averaged expressions are of use in many situations, it should be mentioned that the assumption of completely free rotation is not always appropriate. Spin-spin coupling via the magnetic dipoles of the unpaired electrons on each molecule could lead to certain intermolecular configurations being energetically favoured if the spin is in turn fixed in the molecular frame through spin-orbit coupling. In this case it would be necessary to consider a quantum-statistical average weighted by the magnetic dipole-dipole interactions. This particular orientating mechanism is peculiar to molecules with unpaired spins. Another possible mechanism which would hinder free rotation, and do so more effectively than the purely magnetic interaction, would be the coupling of permanent electric dipole moments. In short, meaningful averaging calculations must take account of all significant coupling mechanisms.

5.2.6 Time reversal characteristics of matrix elements

The discriminatory and non-discriminatory parts of the complete potential are a function of both time-even and time-odd contributions which may be identified by noting from (5.19) and (5.37) that

$$E_{m_1m_2,n_1n_2} \propto \int_0^\infty [a(u,\mathbf{R})(\tilde{\alpha}_{1_{\alpha\beta}})^+_{mn}(iu)(\tilde{\alpha}_{2_{\gamma\delta}})^+_{mn}(iu) + b(u,\mathbf{R})(\tilde{\alpha}_{1_{\alpha\beta}})^-_{mn}(iu)(\tilde{\alpha}_{2_{\gamma\delta}})^-_{mn}(iu)]du \tag{5.53a}$$

and

$$E'_{m_1m_2,n_1n_2} \propto \int_0^\infty [c(u,\mathbf{R})(\tilde{G}_{1_{\alpha\beta}})^+_{mn}(iu)(\tilde{G}_{2_{\gamma\delta}})^+_{mn}(iu) + d(u,\mathbf{R})(\tilde{G}_{1_{\alpha\beta}})^-_{mn}(iu)(\tilde{G}_{2_{\gamma\delta}})^-_{mn}(iu)]du \tag{5.53b}$$

From (5.21) and (5.38), the leading terms of the non-discriminatory and discriminatory parts in the wave-zone are a function of the static limits of $(\tilde{\alpha}_{\alpha\beta})^+_{mn}(\omega)$ and $(\tilde{G}_{\alpha\beta})^+_{mn}(\omega)$ for each molecule. (It is clear that there can be no static limit of $(\tilde{\alpha}_{\alpha\beta})^-_{mn}(\omega)$ and $(\tilde{G}_{\alpha\beta})^-_{mn}(\omega)$). Therefore, to a first approximation, the non-discriminatory interaction consists of purely time-even parts, while the discriminatory interaction consists of purely time-odd parts. These leading terms are dependent on R^{-7}. A more rigorous calculation of the discriminatory dispersion energy in the wave-zone gives (5.40) which reveals a further term, dependent on R^{-9} and composed of both time-odd and time-even parts. This explains the apparent asymmetry in form of the previously predicted expressions for the discriminatory and non-discriminatory energies in the wave-zone. Clearly, if time-odd contributions are forbidden, which is a valid assumption for ground state even-electron systems, the leading terms in the discriminatory and non-discriminatory interactions are dependent on R^{-9} and R^{-7} respectively.

5.3 Discussion

Most theoretical treatments to date have been concerned with small molecule interactions, based on the assumption of one point chiral field per molecule. Yet, the most striking and effective examples of chiral discrimination are to be found in biomolecules. Such molecules are often in possession of many localised chiral centres sometimes combined with a delocalised chirality associated with secondary helical structure. It is easy to see that the former type of chirality may be treated as an extension of the simple two-centre interaction discussed here, where a summation over pairwise interactions would be necessary to determine the intermolecular or intramolecular discriminatory dispersion energy. The latter type of chirality requires a different approach, not dependent on point chiral sources. Craig and Schipper have addressed the problem of what they call environmental chirality, that is chirality resulting from the helical disposition of individual sites which may be locally achiral [56]. They suggest a model in which a small test system interacts with the chiral field produced by a lattice of moments which simulate the helical structure of the biomolecule. In biosystems the relevant localised chiral entities are functional groups attached to a macromolecular framework. For such groups anchored to a large molecule, freedom of movement of one group relative to another can be severely restricted, even for wave-zone separations. This consideration, along with the fact that many biochemical processes involve the formation of radicals, underlines the potential importance in the biological context of the fixed orientation expressions here developed. In particular, the novel time-odd term in R^{-7} in the discriminatory dispersion interaction in the wave-zone may be significant in odd-electron systems, possibly orders of magnitude larger than the spin-independent term in R^{-9}.

In conclusion, it should be emphasized that our treatment is not applicable to the ubiquitous substrate-receptor 'lock and key' type of interaction, for which the proximity of the interacting molecules requires that the actual physical extension of

the molecules be taken into account, invalidating the point chiral source assumption. For such cases, a development of the model proposed by Craig and Schipper would seem germane.

Appendix A

The irreducible spherical tensor notation provides an elegant alternative to the Cartesian formalism, and is particularly suitable for the concise expression of higher order interactions between a molecule and its environment. Use of the notation allows full advantage to be taken of the simpler rotational transformation properties of irreducible spherical tensor components and of the Wigner-Eckart theorem [28,29,31]. This theorem facilitates the evaluation of a general matrix element of an irreducible tensor operator by expressing it as the product of a $3-j$ symbol which describes entirely the dependence of the general matrix element on its component indices and a reduced matrix element which is independent of transformation properties. Let $\hat{T}^k_q$ be an irreducible spherical tensor operator of rank k and component index q which operates within a system with eigenstates $|n, JM\rangle$ where J, M are the angular momentum quantum numbers and n represents any other quantum numbers required to specify the state, then, from the Wigner-Eckart theorem [33,34]

$$\langle n, JM \mid \hat{T}^k_q \mid n', J'M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle n, J \mid\mid \hat{T}^k \mid\mid n', J' \rangle \qquad \text{(A.1)}$$

A modification of the Wigner-Eckart theorem for axially symmetric systems with rotational states characterised by quantum numbers J, K and M is given by (1.16). An irreducible tensor operator $\hat{T}^k_q$ can be constructed from tensor operators $\hat{T}(1)^{k_1}$

and $\hat{T}(2)^{k_2}$ using [26]

$$[\hat{T}(1)^{k_1} \times \hat{T}(2)^{k_2}]^k_q = \sum_{q_1 q_2} (-1)^{k_1 - k_2 - q} (2k+1)^{\frac{1}{2}} \times \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} \hat{T}(1)^{k_1}_{q_1} \hat{T}(2)^{k_2}_{q_2} \tag{A.2}$$

Since the Cartesian coordinates (or angular momentum components) transform under a rotation such that they span the $\mathcal{D}^1$ irreducible representation of the rotation group, it follows that the nine components of a general second rank tensor transform as

$$\mathcal{D}^1 \otimes \mathcal{D}^1 = \mathcal{D}^0 + \mathcal{D}^1 + \mathcal{D}^2 \tag{A.3}$$

and the 27 components of a general third rank tensor as

$$\mathcal{D}^1 \otimes \mathcal{D}^1 \otimes \mathcal{D}^1 = \mathcal{D}^0 + 3\mathcal{D}^1 + 2\mathcal{D}^2 + \mathcal{D}^3 \tag{A.4}$$

Sets of irreducible components for general first and second rank tensors are readily available in the literature. To construct sets of irreducible components for a general third rank tensor we could make use of (A.2) with $k_1 = 1$ and $k_2 = 0, 1, 2$. However, the third rank optical activity tensor operator $\hat{A}_{\alpha\beta\gamma}$ with which we are concerned is, as a consequence of the symmetry properties of the quadrupole moment, symmetric and traceless in its last two subscripts. A second rank symmetric traceless tensor spans exclusively the $\mathcal{D}^2$ part of $\mathcal{D}^1 \otimes \mathcal{D}^1$. Thus by taking $k_1 = 1$ and only $k_2 = 2$ in (A.2) we may obtain the complete set of 15 independent components for $\hat{A}_{\alpha\beta\gamma}$.

In specialising to a third rank tensor with the symmetry properties of $\hat{A}_{\alpha\beta\gamma}$ we note, from

$$\mathcal{D}^1 \otimes \mathcal{D}^2 = \mathcal{D}^1 + \mathcal{D}^2 + \mathcal{D}^3 \tag{A.5}$$

that the degeneracies in $\mathcal{D}^1$ and $\mathcal{D}^2$ are removed and $\mathcal{D}^0$ vanishes.

Although Gray and Lo have constructed spherical components from the Cartesian components of $\hat{A}_{\alpha\beta\gamma}$, the results are presented in reducible, and therefore not immediately useful, form [29].

A.1 Irreducible sets of tensor components

The required sets of irreducible spherical components for the third rank tensor operator $\hat{A}_{\alpha\beta\gamma}$ are presented. For completeness, sets for first and second rank tensors are also listed. We choose to write these in terms of a common example of each tensor type. Thus, the electric dipole operator $\hat{\mu}_\alpha$ exemplifies a first rank tensor operator and the polarizability operator $\hat{\alpha}_{\alpha\beta}$ exemplifies a second rank tensor operator. However, these first and second rank sets are completely general and may be used for any tensor operator of appropriate rank. Specifically, the sets for the optical activity tensor $\hat{G}_{\alpha\beta}$ are identical in form to those given for $\hat{\alpha}_{\alpha\beta}$.

It should be mentioned that the usual statement of the Condon and Shortley phase convention

$$Y^{\ell}_{-m} = (-1)^m Y^{\ell *}_m \tag{A.6}$$

is replaced for spherical tensor components by the relation

$$T^{\ell}_{-m} = (-1)^{n+\ell-m} T^{\ell *}_m \tag{A.7}$$

where n is the rank of the associated Cartesian tensor, which follows from (1.2) and (2.1) in Stone's paper on the construction of irreducible tensor components [28].

First rank tensor:

$$\mu^1_1 = -\frac{1}{\sqrt{2}}(\mu_x + i\mu_y) \tag{A.8a}$$

$$\mu^1_0 = \mu_z \tag{A.8b}$$

$$\mu^1_{-1} = \frac{1}{\sqrt{2}}(\mu_x - i\mu_y) \tag{A.8c}$$

Second rank tensor:

$$\alpha^0_0 = -\frac{1}{\sqrt{3}}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{A.9a}$$

$$\alpha^1_1 = -\frac{1}{2}[\alpha_{xz} - \alpha_{zx} + i(\alpha_{yz} - \alpha_{zy})] \tag{A.9b}$$

$$\alpha^1_0 = \frac{i}{\sqrt{2}}(\alpha_{xy} - \alpha_{yx}) \tag{A.9c}$$

$$\alpha^1_{-1} = -\frac{1}{2}[\alpha_{xz} - \alpha_{zx} - i(\alpha_{yz} - \alpha_{zy})] \quad \text{(A.9d)}$$

$$\alpha^2_2 = \frac{1}{2}[\alpha_{xx} - \alpha_{yy} + i(\alpha_{yx} + \alpha_{xy})] \quad \text{(A.9e)}$$

$$\alpha^2_1 = -\frac{1}{2}[\alpha_{xz} + \alpha_{zx} + i(\alpha_{yz} + \alpha_{zy})] \quad \text{(A.9f)}$$

$$\alpha^2_0 = \frac{1}{\sqrt{6}}[2\alpha_{zz} - (\alpha_{xx} + \alpha_{yy})] \quad \text{(A.9g)}$$

$$\alpha^2_{-1} = \frac{1}{2}[\alpha_{xz} + \alpha_{zx} - i(\alpha_{yz} + \alpha_{zy})] \quad \text{(A.9h)}$$

$$\alpha^2_{-2} = \frac{1}{2}[\alpha_{xx} - \alpha_{yy} - i(\alpha_{yx} + \alpha_{xy})] \quad \text{(A.9i)}$$

Third rank tensor:

$$A^1_1 = \sqrt{\frac{3}{10}}[A_{yyx} - A_{xyy} + A_{zzx} - A_{xzz} + i(A_{xxy} - A_{yxx} + A_{zzy} - A_{yzz})] \quad \text{(A.10a)}$$

$$A^1_0 = \sqrt{\frac{3}{5}}[A_{zxx} - A_{xxz} + A_{zyy} - A_{yyz}] \quad \text{(A.10b)}$$

$$A^1_{-1} = -\sqrt{\frac{3}{10}}[A_{yyx} - A_{xyy} + A_{zzx} - A_{xzz} - i(A_{xxy} - A_{yxx} + A_{zzy} - A_{yzz})] \quad \text{(A.10c)}$$

$$A^2_2 = \frac{1}{\sqrt{6}}[A_{xxz} - A_{zxx} + A_{zyy} - A_{yyz} - i(2A_{zxy} - A_{xyz} - A_{yzx})] \quad \text{(A.10d)}$$

$$A^2_1 = \frac{1}{\sqrt{6}}[A_{xyy} - A_{yyx} + A_{zzx} - A_{xzz} + i(A_{yxx} - A_{xxy} + A_{zzy} - A_{yzz})] \quad \text{(A.10e)}$$

$$A^2_0 = i(A_{xyz} - A_{yzx}) \quad \text{(A.10f)}$$

$$A^2_{-1} = \frac{1}{\sqrt{6}}[A_{xyy} - A_{yyx} + A_{zzx} - A_{xzz} - i(A_{yxx} - A_{xxy} + A_{zzy} - A_{yzz})] \quad \text{(A.10g)}$$

$$A^2_{-2} = -\frac{1}{\sqrt{6}}[A_{xxz} - A_{zxx} + A_{zyy} - A_{yyz} + i(2A_{zxy} - A_{xyz} - A_{yzx})] \quad \text{(A.10h)}$$

$$A^3_3 = \frac{1}{2\sqrt{2}}[2A_{yyx} + 2A_{xyy} + A_{xzz} - i(2A_{xxy} + 2A_{yxx} + A_{yzz})] \quad \text{(A.10i)}$$

$$A^3_2 = \frac{1}{2\sqrt{3}}[2A_{xxz} + A_{zxx} - 2A_{yyz} - A_{zyy}$$

$$+2i(A_{xyz}+A_{yzx}+A_{zxy})] \tag{A.10j}$$

$$A_1^3 = \frac{1}{2\sqrt{30}}[2A_{yyx}-2A_{xyy}-7A_{xzz}-8A_{zzx}$$
$$+i(2A_{xxy}-2A_{yxx}-7A_{yzz}-8A_{zzy})] \tag{A.10k}$$

$$A_0^3 = -\frac{1}{\sqrt{10}}(3A_{zxx}+2A_{xxz}+3A_{zyy}+2A_{yyz}) \tag{A.10l}$$

$$A_{-1}^3 = -\frac{1}{2\sqrt{30}}[2A_{yyx}-2A_{xyy}-7A_{xzz}-8A_{zzx}$$
$$-i(2A_{xxy}-2A_{yxx}-7A_{yzz}-8A_{zzy})] \tag{A.10m}$$

$$A_{-2}^3 = \frac{1}{2\sqrt{3}}[2A_{xxz}+A_{zxx}-2A_{yyz}-A_{zyy}$$
$$-2i(A_{xyz}+A_{yzx}+A_{zxy})] \tag{A.10n}$$

$$A_{-3}^3 = -\frac{1}{2\sqrt{2}}[2A_{yyx}+2A_{xyy}+A_{xzz}$$
$$+i(2A_{xxy}+2A_{yxx}+A_{yzz})] \tag{A.10o}$$

References

1. Barron, L. D., 1982, *Molecular Light Scattering and Optical Activity*, (Cambridge University Press).

2. Mason, S. F., 1982, *Molecular Optical Activity and the Chiral Discriminations*, (Cambridge University Press).

3. Mason, S. F. (editor), 1979, *Optical Activity and Chiral Discrimination*, (Reidel).

4. Barron, L. D., 1978, *Advances in Infrared and Raman Spectroscopy*, **4**, R. J. H. Clark and R. E. Hester (editors), (Heyden), p.271.

5. Nafie, L. A., 1984, *Advances in Infrared and Raman Spectroscopy*, **11**, R. J. H. Clark and R. E. Hester (editors), (Heyden), p.49.

6. Chiu, Y. N., 1970, *J. Chem. Phys.*, **52**, 1042.

7. Salzman, W. R., 1974, *Chem. Phys. Lett.*, **25**, 302.

8. Salzman, W. R., 1977, *J. Chem. Phys.*, **67**, 291.

9. Salzman, W. R., 1987, *Chem. Phys. Lett.*, **134**, 622.

10. Barron, L. D. and Johnston, C. J., 1985, *J. Ram. Spec.*, **16**, 208.

11. Polavarapu, P. L., 1987, *J. Chem. Phys.*, **86** 1136.

12. Barron, L. D. and Buckingham, A. D., 1971, *Mol. Phys.*, **20**, 1111.

13. Buckingham, A. D., 1967, *Adv. Chem. Phys.*, **12**, 107.

14. Barron, L. D., 1981, *Mol. Phys.*, **43**, 1395.

15. Barron, L. D. and Nørby-Svendsen, E., 1981, *Advances in Infrared and Raman Spectroscopy*, **8**, R. J. H. Clark and R. E. Hester (editors), (Heyden), p.322.

16. Koningstein, J. A., 1972, *Introduction to the Theory of the Raman Effect*, (Reidel).

17. Weber, A., 1973, *The Raman Effect*, **2**, A. Anderson (editor), (Marcel Dekker), p.543.

18. Hamaguchi, H., 1985, *Advances in Infrared and Raman Spectroscopy*, **12**, R. J. H. Clark and R. E. Hester (editors), (Wiley Heyden),p.273.

19. Spiro, T. G. and Strekas, T. C., 1972, *Proc. Natn. Acad. Sci. USA*, **69**, 2622.

20. Hamaguchi, H., Harada, I. and Shimanouchi, T., 1975, *Chem. Phys. Lett.*, **32**, 103.

21. Ghandour, F., Jacon, M., Nørby Svendsen, E. and Oddershede, J., 1983, *J. Chem. Phys.*, **79**, 2150.

22. Holzer, W., Murphy, W. F., Bernstein, H. J., 1970, *J. Chem. Phys.*, **52**, 399.

23. Herzberg, G., 1950, *Spectra of Diatomic Molecules*, (D. van Nostrand Company).

24. Zeigler, L. D., 1986, *J. Chem. Phys.*, **84**, 6013.

25. Bunker, P. R., 1979, *Molecular Symmetry and Spectroscopy*, (Academic Press).

26. Silver, B. L., 1976, *Irreducible Tensor Methods*, (Academic Press).

27. Edmonds, A. R., 1960, *Angular Momentum in Quantum Mechanics*, (Princeton University Press).

28. Stone, A. J., 1975, *Mol. Phys.*, **29**, 1461.

29. Gray, C. G. and Lo, B. W. N., 1976, *Chem. Phys.*, **14**, 73.

30. Placzek, G. and Teller, E., 1933, Z. Physik, **81**, 209.

31. Altmann, K. and Strey, G., 1972, *J. Mol. Spectrosc.*, **44**, 571.

32. Papoušek D. and Aliev, M. R., 1982, *Molecular Vibrational-Rotational Spectra*, (Elsevier).

33. Berestetskii, V. B., Lifshitz, E. M. and Pitaevskii, L. P., 1971, *Relativistic Quantum Theory, Part 1*, (Pergamon Press).

34. Landau L. D. and Lifshitz, E. M., 1977, *Quantum Mechanics, 3rd ed.*, (Pergamon Press).

35. Gaufres, R. and Sportouch, S., 1971, *J. Mol. Spectrosc.*, **39**, 527.

36. Stoicheff, B. P., *Infrared and Raman Spectra*, (D. van Nostrand Company).

37. Bogaard, M. P. and Orr, B. J., 1974, *M. T. P. Review of Molecular Structure and Properties*, Series 2, A. D. Buckingham (editor), (Butterworth).

38. Barron, L. D., 1981, *Chem. Phys. Lett.*, **79**, 392.

39. Barron, L. D., 1986, *Chem. Phys. Lett.*, **123**, 423.

40. Murphy, W. F., 1981, *J. Ram. Spec.*, **11**, 339.

41. Allen Jr., H. C. and Cross, P. C., 1963, *Molecular Vib-Rotors*, (Wiley).

42. Townes, C. H. and Schawlow, A. L., 1955, *Microwave Spectroscopy*, (McGraw-Hill).

43. Kiefer W. and Long, D. A., 1982, *Non-linear Raman Spectroscopy and its Chemical Applications*, (Riedel).

44. Schneider, F. W., *Proceedings of the Second European Conference on the Spectroscopy of Biological Molecules*, (to be published), University of Freiburg, 1987.

45. Buckingham, A. D. and Dunn, M. B., 1971, *J. Chem. Soc. A*, 1988.

46. Chui, Y. N., Kenney, A. V. and Brown, S. H., 1980, *J. Chem. Phys.*, **73**, 1422.

47. Dence, J. B., 1975, *Mathematical Techniques in Chemistry*, (John Wiley and Sons).

48. Wollrab, J. E., 1967, *Rotational Spectra and Molecular Structure*, (Academic Press).

49. Eshbach, J. R. and Strandberg, M. W. P., 1952, *Phys. Rev.*, **85**, 24.

50. Atkins, P. W. and Gomes, J. A. N. F., *Chem. Phys. Lett.*, 1976, **39**, 519.

51. Polavarapu, P. L. and Michalska, D. F., 1983, *J. Am. Chem. Soc.*, **105**, 6190.

52. Craig, D. P. and Mellor, D. P., 1976, *Topics Curr. Chem.*, **63**, 1.

53. Mavroyannis, C and Stephen, M. J., 1962, *Molec. Phys.*, **5**, 629.

54. Craig, D. P., Power, E. A. and Thirunamachandran, T., 1970, *Chem. Phys. Lett.*, **6**, 211.

55. Craig, D. P., Power, E. A. and Thirunamachandran, T., 1971, *Proc. R. Soc. London A*, **322**, 165.

56. Craig, D. P. and Schipper, P. E., 1975, *Proc. R. Soc. London A*, **342**, 19.

57. Kuroda, R., Mason, S. F., Rodger, C. D. and Seal, R. H., 1978, *Chem. Phys. Letts.*, **57**, 1.

58. Power E. A. and Thirunamachandran, T., 1986, *Int. Rev. Phys. Chem.*, **5**, 273.

59. Buckingham, A. D., 1979, *Phil. Trans. R. Soc. A*, **293**, 239.

60. Buckingham, A. D., and Joslin, C. G., 1981, *Chem. Phys. Lett.*, **80**, 615.

61. Craig, D. P. and Thirunamachandran, T., 1984, *Molecular Quantum Electrodynamics*, (Academic Press).

62. Buckingham, A. D., 1978, *Intermolecular Interactions*, Pullman, B. (editor), (Wiley), p.1.

63. Henning, G. N., McCaffery, A. J., Schatz, P. N. and Stephens P. J., 1968, *J. Chem. Phys.*, **48**, 5656.

64. Harnung, S. E., 1973, *Molec. Phys.*, **26**, 473.

65. Piepho, S. B. and Schatz, P. N., 1983, *Group Theory in Spectroscopy*, (Wiley), p.488.

66. Feynman, R. P., *Quantum Electrodymanics*, (W. A. Benjamin Inc.).

67. Casimir, H. B. and Polder, D., 1948, *Phys. Rev.*, **73**, 360.

Publications

Rotational Raman Optical Activity in Chiral Symmetric Tops

L. D. Barron and C. J. Johnston
Chemistry Department, The University, Glasgow G12 8QQ, UK

A theory of rotational Raman optical activity in chiral symmetric top molecules is presented. The required rotational transition polarizability and optical activity tensors are calculated using irreducible tensor methods for axially symmetric systems. Selection rules on optically active rotational Raman scattering are found to be basically the same as for conventional rotational Raman scattering, namely $\Delta J = 0, \pm 1, \pm 2$ with $\Delta K = 0$, but in addition to possessing an anisotropic polarizability, the molecule must be chiral and must possess an anisotropy in the electronic optical activity tensors. A measure of this optical activity anisotropy is provided by the dimensionless circular intensity difference in a resolved rotational Raman band or in the envelope of unresolved bands provided the envelope is resolved from the central sharp Rayleigh line. A group polarizability model is used to calculate the rotational Raman optical activity in a chiral (D_3) conformation of triphenylborane.

INTRODUCTION

In the past decade, conventional natural optical activity measurements, associated with electronic transitions of chiral molecules, have been augmented with vibrational optical activity measurements using both infrared circular dichroism (IRCD)[1-4] and Raman optical activity (ROA).[5-8] The former measures a small difference in the absorption of left and right circularly polarized infrared radiation, the latter a small difference in the Raman scattering of right and left circularly polarized visible radiation, and both provide detailed and complementary new stereochemical information. It is now time to discuss the further possibility of optical activity in pure rotational transitions.

Although rotational structure has been seen in gas-phase vibrational IRCD spectra,[9] it is not likely that IRCD will yield pure rotational optical activity spectra, since the lowest frequency so far reached is *ca* 600 cm^{-1}.[10] On the other hand, the Raman approach, since it excites with visible light, suffers no frequency limitations and so pure rotational Raman optical activity measurements should be feasible, given the right sample. Here we present a model calculation of rotational ROA in a chiral symmetric top molecule.

Even though they cannot usually be applied directly to an actual chiral molecule, simple models have been of great value in the development of theories of conventional electronic and vibrational optical activity since they provide physical insight into the generation of the phenomena by archetypal chiral structures and often serve as the basis for more sophisticated theories.[11] The chiral symmetric top serves this purpose for theories of rotational optical activity, which justifies the detailed development below even though suitable chiral symmetric top molecules are rare so that the explicit results are likely to have limited direct applicability. However, since the rotational states of asymmetric top molecules are written in a symmetric top basis, the results provide a first step towards the calculation of rotational ROA in chiral asymmetric tops, which is likely to be more important from the experimental standpoint.

The results also illuminate a fundamental problem in the theory of the quantum states of chiral objects. It has been suggested that rotating achiral molecules, even symmetric or spherical tops, are optically active,[12,13] with counter-rotating pairs constituting enantiomers.[14] This view has been criticized by applying the fundamental symmetry operations of space inversion and time reversal to the corresponding rotational quantum states, which shows that rotating achiral molecules are not truly chiral objects.[11,15,16] If an achiral molecule prepared in a pure rotational quantum state can be properly regarded as a chiral object, it should support the pseudo-scalar rotational ROA observable. However, our results show that this is definitely not the case: the rotational quantum states by themselves introduce no new source of chirality. (The optical rotation observable invoked in Refs 12-14 is actually magnetic, or Faraday, rotation which is a time-odd axial vector and so is completely different from the natural optical rotation observable, which is a time-even pseudo-scalar. There will be a corresponding magnetic ROA observable that can be supported by rotating achiral molecules, but this is not considered here.)

THEORY

The circular intensity difference

Most of the material of this and the next sub-section has already been given elsewhere (see the detailed references for the various formulae), but is included here for completeness.

Our measure of Rayleigh and Raman optical activity is a dimensionless circular intensity difference (CID) given by

$$\Delta_\alpha = (I_\alpha^R - I_\alpha^L)/(I_\alpha^R + I_\alpha^L) \qquad (1)$$

where I_α^R and I_α^L are scattered intensities with α-polarization in right and left circularly polarized incident light (see Refs 17 and 18 for a discussion of other conventions). The CIDs have been developed in terms of

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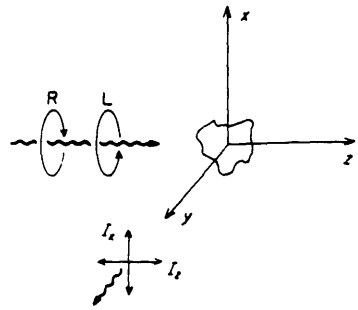


Figure 1. The geometry for polarized light scattering at 90°.

molecular property tensors by using a semi-classical theory in which the origin of scattered light is considered to be the fields radiated by the electric and magnetic multipole moments induced in a molecule by the incident light wave. For a plane-wave light beam of angular frequency ω incident along the z direction and scattered at 90° along y (Fig. 1), the polarized (x) and depolarized (z) Rayleigh circular intensity sums and differences are found to be[11,19,20]

$$I_x^R + I_x^L = \frac{\omega^4 \mu_0 E^{(0)2}}{32\pi^2 cy^2} (\tilde{\alpha}_{xx}\tilde{\alpha}^*_{xx} + \tilde{\alpha}_{xy}\tilde{\alpha}^*_{xy} + \cdots) \quad (2a)$$

$$I_z^R + I_z^L = \frac{\omega^4 \mu_0 E^{(0)2}}{32\pi^2 cy^2} (\tilde{\alpha}_{zx}\tilde{\alpha}^*_{zx} + \tilde{\alpha}_{zy}\tilde{\alpha}^*_{zy} + \cdots) \quad (2b)$$

$$I_x^R - I_x^L = \frac{\omega^4 \mu_0 E^{(0)2}}{16\pi^2 c^2 y^2} [\mathrm{Im}\,(c\tilde{\alpha}_{xy}\tilde{\alpha}^*_{xx} + \tilde{\alpha}_{xy}\tilde{G}^*_{xy} + \tilde{\alpha}_{xx}\tilde{G}^*_{xx} - \tilde{\alpha}_{xy}\tilde{\mathcal{G}}^*_{xz} + \tilde{\alpha}_{xx}\tilde{\mathcal{G}}^*_{yz}) + \tfrac{1}{3}\omega\,\mathrm{Re}\,(\tilde{\alpha}_{xx}\tilde{A}^*_{xzy} - \tilde{\alpha}_{xy}\tilde{A}^*_{zzx} + \tilde{\alpha}_{xy}\tilde{\mathcal{A}}^*_{xxy} - \tilde{\alpha}_{xx}\tilde{\mathcal{A}}^*_{yxy}) + \cdots] \quad (2c)$$

$$I_z^R - I_z^L = \frac{\omega^4 \mu_0 E^{(0)2}}{16\pi^2 c^2 y^2} [\mathrm{Im}\,(c\tilde{\alpha}_{zy}\tilde{\alpha}^*_{zx} + \tilde{\alpha}_{zy}\tilde{G}^*_{zy} + \tilde{\alpha}_{zx}\tilde{G}^*_{zx} + \tilde{\alpha}_{zy}\tilde{\mathcal{G}}^*_{xx} - \tilde{\alpha}_{zx}\tilde{\mathcal{G}}^*_{yx}) + \tfrac{1}{3}\omega\,\mathrm{Re}\,(\tilde{\alpha}_{zx}\tilde{A}^*_{zzy} - \tilde{\alpha}_{zy}\tilde{A}^*_{zzx} + \tilde{\alpha}_{zy}\tilde{\mathcal{A}}^*_{xzy} - \tilde{\alpha}_{zx}\tilde{\mathcal{A}}^*_{yzy}) + \cdots] \quad (2d)$$

The complex polarizability and optical activity tensors are written as sums of real (unprimed) and imaginary (primed) parts:

$$\tilde{\alpha}_{\alpha\beta} = \alpha_{\alpha\beta} - i\alpha'_{\alpha\beta} \quad (3a)$$

$$\tilde{G}_{\alpha\beta} = G_{\alpha\beta} - iG'_{\alpha\beta} \quad (3b)$$

$$\tilde{A}_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} - iA'_{\alpha\beta\gamma} \quad (3c)$$

$$\tilde{\mathcal{G}}_{\alpha\beta} = G_{\alpha\beta} + iG'_{\alpha\beta} \quad (3d)$$

$$\tilde{\mathcal{A}}_{\alpha\beta\gamma} = A_{\alpha\beta\gamma} + iA'_{\alpha\beta\gamma} \quad (3e)$$

A tilde ($\sim$) denotes a complex quantity. Time-dependent perturbation theory provides the following quantum mechanical expressions:[11,21]

$$\alpha_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\,\mathrm{Re}\,(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) \quad (4a)$$

$$\alpha'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\,\mathrm{Im}\,(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) \quad (4b)$$

$$G_{\alpha\beta} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\,\mathrm{Re}\,(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle) \quad (4c)$$

$$G'_{\alpha\beta} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\,\mathrm{Im}\,(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle) \quad (4d)$$

$$A_{\alpha\beta\gamma} = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\,\mathrm{Re}\,(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle) \quad (4e)$$

$$A'_{\alpha\beta\gamma} = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\,\mathrm{Im}\,(\langle n|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle) \quad (4f)$$

where $\omega_{jn} = \omega_j - \omega_n$, and μ_α, m_α and $\Theta_{\alpha\beta}$ are the electric dipole, magnetic dipole and traceless electric quadrupole moment operators, respectively, defined by

$$\mu_\alpha = \sum_i e_i r_{i_\alpha} \quad (5a)$$

$$m_\alpha = \sum_i \frac{e_i}{2m_i}\varepsilon_{\alpha\beta\gamma} r_{i_\beta} p_{i_\gamma} \quad (5b)$$

$$\Theta_{\alpha\beta} = \tfrac{1}{2}\sum_i e_i(3r_{i_\alpha}r_{i_\beta} - r_i^2\delta_{\alpha\beta}) \quad (5c)$$

particle i at $\mathbf{r}_i$ having charge e_i and linear momentum $\mathbf{p}_i$ (we use a cartesian tensor notation in which $\delta_{\alpha\beta}$ is the unit symmetric second-rank tensor, $\varepsilon_{\alpha\beta\gamma}$ is the unit antisymmetric third-rank tensor and a repeated Greek suffix in the same term denotes a summation over the Cartesian components[11]).

If the initial state $|n\rangle$ is non-degenerate, and no static external magnetic fields are present, it can be shown from time reversal arguments that only $\alpha_{\alpha\beta}$, $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$ survive [see Eqns (11) below]. For scattering from isotropic fluids it is necessary to average Eqns (2) over all orientations of the chiral molecule, and the corresponding polarized and depolarized Rayleigh CIDs are found to be[11,19]

$$\Delta_x(90°) = \frac{2(7\alpha_{\alpha\beta}G'^*_{\alpha\beta} + \alpha_{\alpha\alpha}G'^*_{\beta\beta} + \frac{1}{3}\omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A^*_{\gamma\delta\beta})}{c(7\alpha_{\lambda\mu}\alpha^*_{\lambda\mu} + \alpha_{\lambda\lambda}\alpha^*_{\mu\mu})} \quad (6a)$$

$$\Delta_z(90°) = \frac{4(3\alpha_{\alpha\beta}G'^*_{\alpha\beta} - \alpha_{\alpha\alpha}G'^*_{\beta\beta} - \frac{1}{3}\omega\alpha_{\alpha\beta}\varepsilon_{\alpha\gamma\delta}A^*_{\gamma\delta\beta})}{2c(3\alpha_{\lambda\mu}\alpha^*_{\lambda\mu} - \alpha_{\lambda\lambda}\alpha^*_{\mu\mu})} \quad (6b)$$

However, we are concerned here with rotational Raman scattering and so must extend the formalism to accommodate transition tensors. Also, the CIDs in specific resolved rotational Raman bands must be calculated in place of the isotropic averages [Eqns (6)], but we shall see that Eqns (6) provide a valuable check on the results.

Rotational Raman transition tensors

The circular intensity sum and difference [Eqns (2)] can be applied to Raman optical activity by replacing the property tensors $\tilde{\alpha}_{\alpha\beta}$, etc. by corresponding transition tensors $(\tilde{\alpha}_{\alpha\beta})_{mn}$, etc., between different initial and final molecular states $|n\rangle$ and $|m\rangle$. These transition tensors have the quantum mechanical forms[11]

$$(\tilde{\alpha}_{\alpha\beta})_{mn} = \frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle}{\omega_{jn} - \omega} + \frac{\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm} + \omega}\right] \quad (7a)$$

$$(\tilde{G}_{\alpha\beta})_{mn}=\frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle}{\omega_{jn}-\omega}+\frac{\langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm}+\omega}\right] \tag{7b}$$

$$(\tilde{A}_{\alpha\beta\gamma})_{mn}=\frac{1}{\hbar}\sum_{j\neq n,m}\left[\frac{\langle m|\mu_\alpha|j\rangle\langle j|\Theta_{\beta\gamma}|n\rangle}{\omega_{jn}-\omega}+\frac{\langle m|\Theta_{\beta\gamma}|j\rangle\langle j|\mu_\alpha|n\rangle}{\omega_{jm}+\omega}\right] \tag{7c}$$

and can be written as follows in terms of explicit real and imaginary parts:

$$(\tilde{\alpha}_{\alpha\beta})_{mn}=(\alpha_{\alpha\beta})_{mn}-i(\alpha'_{\alpha\beta})_{mn} \tag{8a}$$

$$\begin{aligned}(\alpha_{\alpha\beta})_{mn}=\frac{1}{2\hbar}\sum_{j\neq n,m}\frac{1}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)}&\times[(\omega_{jn}+\omega_{jm})\,\mathrm{Re}\,(\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\\&+\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle)+(2\omega+\omega_{nm})\\&\times\mathrm{Re}\,(\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\\&-\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle)]\end{aligned} \tag{8b}$$

$$\begin{aligned}(\alpha'_{\alpha\beta})_{mn}=-\frac{1}{2\hbar}\sum_{j\neq n,m}\frac{1}{(\omega_{jn}-\omega)(\omega_{jm}+\omega)}&\times[(\omega_{jn}+\omega_{jm})\,\mathrm{Im}\,(\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\\&+\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle)+(2\omega+\omega_{nm})\\&\times\mathrm{Im}\,(\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle\\&-\langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle)]\end{aligned} \tag{8c}$$

with similar expressions for $(\tilde{G}_{\alpha\beta})_{mn}$ and $(\tilde{A}_{\alpha\beta\gamma})_{mn}$ in which μ_β is replaced by m_β and $\Theta_{\beta\gamma}$, respectively.

These transition tensors can be generated by taking matrix elements of corresponding effective operators.[11,16,22] Thus the effective polarizability operator is

$$\hat{\alpha}_{\alpha\beta}=\hat{\alpha}^{+}_{\alpha\beta}+\hat{\alpha}^{-}_{\alpha\beta} \tag{9a}$$

$$\hat{\alpha}^{+}_{\alpha\beta}=\tfrac{1}{2}(\mu_\alpha O^{+}\mu_\beta+\mu_\beta O^{+}\mu_\alpha) \tag{9b}$$

$$\hat{\alpha}^{-}_{\alpha\beta}=-\tfrac{1}{2}(\mu_\alpha O^{-}\mu_\beta-\mu_\beta O^{-}\mu_\alpha) \tag{9c}$$

where

$$O^{\pm}=\left(\frac{1}{H-\bar{W}+\hbar\omega}\pm\frac{1}{H-\bar{W}-\hbar\omega}\right) \tag{9d}$$

$\bar{W}$ is the average of the energies W_n and W_m of the initial and final states. By summing over a complete set of states $|j\rangle\langle j|$ inserted after O, and using the approximation $\omega_{jn}\approx\omega_{jm}$, it is easily verified that $\langle m|\alpha_{\alpha\beta}|n\rangle$ generates the complex transition polarizability $(\tilde{\alpha}_{\alpha\beta})_{mn}$ [Eqn (7a)]. Similarly, the effective optical activity operators are

$$\hat{G}_{\alpha\beta}=\hat{G}^{+}_{\alpha\beta}+\hat{G}^{-}_{\alpha\beta} \tag{10a}$$

$$\hat{G}^{+}_{\alpha\beta}=\tfrac{1}{2}(\mu_\alpha O^{+}m_\beta+m_\beta O^{+}\mu_\alpha) \tag{10b}$$

$$\hat{G}^{-}_{\alpha\beta}=-\tfrac{1}{2}(\mu_\alpha O^{-}m_\beta-m_\beta O^{-}\mu_\alpha) \tag{10c}$$

$$\hat{A}_{\alpha\beta\gamma}=\hat{A}^{+}_{\alpha\beta\gamma}+\hat{A}^{-}_{\alpha\beta\gamma} \tag{10d}$$

$$\hat{A}^{+}_{\alpha\beta\gamma}=\tfrac{1}{2}(\mu_\alpha O^{+}\Theta_{\beta\gamma}+\Theta_{\beta\gamma}O^{+}\mu_\alpha) \tag{10e}$$

$$\hat{A}^{-}_{\alpha\beta\gamma}=-\tfrac{1}{2}(\mu_\alpha O^{-}\Theta_{\beta\gamma}-\Theta_{\beta\gamma}O^{-}\mu_\alpha) \tag{10f}$$

(The notation for these operators is slightly different to that in Refs 11, 16 and 22; also we have corrected some sign errors.)

These effective polarizability and optical activity operators have certain well defined characteristics:[11,16,22] thus $\hat{\alpha}^{+}_{\alpha\beta}$ is Hermitian, has even parity and is time-even; $\hat{\alpha}^{-}_{\alpha\beta}$ is anti-Hermitian, has even parity and is time-odd; $\hat{G}^{+}_{\alpha\beta}$ is Hermitian, has odd parity and is time-odd; $\hat{G}^{-}_{\alpha\beta}$ is anti-Hermitian, has odd parity and is time-even; $\hat{A}^{+}_{\alpha\beta\gamma}$ is Hermitian, has odd parity and is time-even; and $\hat{A}^{-}_{\alpha\beta\gamma}$ is anti-Hermitian, has odd parity and is time-odd. This classification is important when considering the various light-scattering and optical activity phenomena that each operator can generate, and leads to the following fundamental properties of the transition tensors:[11,16,22]

$$\langle m|\hat{\alpha}_{\alpha\beta}|n\rangle=\langle\Theta n|\hat{\alpha}_{\beta\alpha}|\Theta m\rangle=\langle\Theta m|\hat{\alpha}_{\alpha\beta}|\Theta n\rangle^{*} \tag{11a}$$

$$\langle m|\hat{G}_{\alpha\beta}|n\rangle=-\langle\Theta m|\hat{G}_{\alpha\beta}|\Theta n\rangle^{*} \tag{11b}$$

$$\langle m|\hat{A}_{\alpha\beta\gamma}|n\rangle=\langle\Theta m|\hat{A}_{\alpha\beta\gamma}|\Theta n\rangle^{*} \tag{11c}$$

where Θ is here the time reversal operator (not to be confused with the electric quadrupole moment). One important consequence of Eqns (11) is that, for an even-electron system, only the real parts $(\alpha_{\alpha\beta})_{mn}$ and $(A_{\alpha\beta\gamma})_{mn}$ of $\langle m|\tilde{\alpha}_{\alpha\beta}|n\rangle$ and $\langle m|\tilde{A}_{\alpha\beta\gamma}|n\rangle$ and the imaginary part $(G'_{\alpha\beta})_{mn}$ of $\langle m|\tilde{G}_{\alpha\beta}|n\rangle$ survive (assuming no static external magnetic field is present). The situation for odd-electron systems is more complicated and will not be elaborated here.

The Born-Oppenheimer approximation is now introduced so that each state is written as a product of electronic, vibrational and rotational parts:

$$|j\rangle=|j_e j_v j_r\rangle=|j_{\mathrm{int}}\,j_r\rangle \tag{12}$$

where $|j_{\mathrm{int}}\rangle$ is the internal molecular vibronic state. In the usual theory of rotational Raman scattering,[23,24] the rotational contributions to the transition frequencies in the transition polarizability are neglected and the closure theorem invoked with respect to the complete set of rotational states associated with every electronic-vibrational state, which enables the transition polarizability to be written[11] (for an even-electron system):

$$\langle m_{\mathrm{int}}m_r|\hat{\alpha}_{\alpha\beta}|n_{\mathrm{int}}n_r\rangle=\langle m_r|(\alpha_{\alpha\beta})_{m_{\mathrm{int}}n_{\mathrm{int}}}|n_r\rangle \tag{13}$$

where

$$\begin{aligned}(\alpha_{\alpha\beta})_{m_{\mathrm{int}}n_{\mathrm{int}}}=\frac{2}{\hbar}\sum_{\substack{j_{\mathrm{int}}\neq\\ m_{\mathrm{int}}n_{\mathrm{int}}}}\frac{\omega_{j_{\mathrm{int}}n_{\mathrm{int}}}}{\omega^2_{j_{\mathrm{int}}n_{\mathrm{int}}}-\omega^2}&\\\times\mathrm{Re}\,(\langle m_{\mathrm{int}}|\mu_\alpha|j_{\mathrm{int}}\rangle\langle j_{\mathrm{int}}|\mu_\beta|n_{\mathrm{int}}\rangle)&\end{aligned} \tag{14}$$

is an internal transition tensor that acts as an operator on the rotational states. The space-fixed axes $\alpha, \beta, \ldots$ can then be related to molecule-fixed axes $\alpha', \beta', \ldots$ using direction cosines such as $l_{\alpha\alpha'}$ between the α and α' axis so that Eqn (13) becomes

$$\langle m_r|(\alpha_{\alpha\beta})_{m_{\mathrm{int}}n_{\mathrm{int}}}|n_r\rangle=(\alpha_{\alpha'\beta'})_{m_{\mathrm{int}}n_{\mathrm{int}}}\langle m_r|l_{\alpha\alpha'}l_{\beta\beta'}|n_r\rangle \tag{15}$$

the rotational transition being effected by the direction cosine operators. A similar development is possible for the transition optical activity tensors. However, the complexity of the rotational Raman optical activity calculation warrants a more sophisticated approach utilizing

Table 1. Rotational Raman factors, $D^1_{J'K',JK}$

	J'		
K'	$J-1$	J	$J+1$
$K-1$	$\frac{(J+K)(J+K-1)}{2J(2J+1)}$	$\frac{(J+K)(J-K+1)}{2J(J+1)}$	$\frac{(J-K+1)(J-K+2)}{2(J+1)(2J+1)}$
K	$\frac{J^2-K^2}{J(2J+1)}$	$\frac{4K^2}{J(J+1)}$	$\frac{[(J+1)^2-K^2]}{(J+1)(2J+1)}$
$K+1$	$\frac{(J-K)(J-K-1)}{2J(2J+1)}$	$\frac{(J-K)(J+K+1)}{2J(J+1)}$	$\frac{(J+K+1)(J+K+2)}{2(J+1)(2J+1)}$

irreducible spherical tensor operators, to which we now turn.

Matrix elements and intensity factors

Symmetric top rotational matrix elements can be obtained by using the following extension of the Wigner-Eckart theorem to axially symmetric systems (within the Condon and Shortley phase convention extended to general spherical tensor components):[25-27]

$$\langle n', J'K'M'|\hat{T}^k_q|n, JKM\rangle = i^{J'+J-K'-K}(-1)^{J'-M'}[(2J'+1)(2J+1)]^{1/2} \times \begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}\begin{pmatrix} J' & k & J \\ -M' & q & M \end{pmatrix} \times \langle n'|\overline{\hat{T}^k_{K'-K}}|n\rangle \quad (16)$$

where J, K, M are the usual set of symmetric top rotational quantum numbers, n denotes the internal (vibrational-electronic) states, and $\hat{T}^k_q$ is the qth component of the rank-k set of tensor operators expressed in irreducible spherical form with respect to space-fixed axes. A bar over the operator indicates that it is defined with respect to molecule-fixed axes, so that $\langle n'|\overline{\hat{T}^k_{K'-K}}|n\rangle$ is an internal matrix element [and would be an analogue, in a spherical basis, of $(\alpha_{\alpha'\beta'})_{m_{\rm int}n_{\rm int}}$ in Eqn (15), for example].

Since we are calculating intensities, and the magnetic substates are degenerate if no external static magnetic field is present, considerable simplification is possible by invoking the following sum:[26]

$$\sum_{M'M}|\langle n', J'K'M'|\hat{T}^k_q|n, JKM\rangle|^2 = \frac{(2J'+1)(2J+1)}{2k+1} \times \begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}^2 |\langle n'|\overline{\hat{T}^k_{K'-K}}|n\rangle|^2 \quad (17)$$

Each of the $2J+1$ values of M in the initial state is equally probable, so the associated "intensity factor" is obtained by dividing Eqn (17) by $(2J+1)$:

$$(I^k_q)_{J'K',JK} = \frac{(2J'+1)}{(2k+1)}\begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}^2 \times |\langle n'|\overline{\hat{T}^k_{K'-K}}|n\rangle|^2 \quad (18)$$

Similar results are given in Refs 23 and 28. We now write

$$(I^k_q)_{J'K',JK} = \frac{1}{2k+1}|\langle n'|\overline{\hat{T}^k_{K'-K}}|n\rangle|^2 D^k_{J'K',JK} \quad (19a)$$

where

$$D^k_{J'K',JK} = (2J'+1)\begin{pmatrix} J' & k & J \\ -K' & K'-K & K \end{pmatrix}^2 \quad (19b)$$

is actually the factor $b^{JK}_{J'K'}$ of Placzek and Teller[29] when $k=2$. This treatment can therefore be correlated with the traditional theory of rotational Raman scattering,[23,24,29-31] except that we can automatically accommodate antisymmetric scattering by taking intensity factors with $k=1$. We require the factors $D^k_{J'K',JK}$ with $k=0, 1, 2$: using the formulae given by Edmonds[32] for the first few $3j$ symbols, we find for $k=0$ that only $D^0_{JK,JK}=1$ is allowed, and for $k=1$ and 2 we find the factors listed in Tables 1 and 2, respectively. The properties of the $3j$ symbol enable the following properties of $D^k_{J'K',JK}$ to be deduced:

$$D^k_{J'K',JK} = D^k_{J'-K',J-K} \quad (20a)$$

$$(2J+1)D^k_{J'K',JK} = (2J'+1)D^k_{JK,J'K'} \quad (20b)$$

$$\sum_{J'} D^k_{J'K',JK} = 1 \quad (20c)$$

$$\sum_{K} D^k_{J'K',JK} = \sum_{K'} D^k_{J'K',JK} = (2J'+1)/(2k+1) \quad \text{(for fixed } \Delta K = K'-K) \quad (20d)$$

Placzek and Teller's factor $b^{JK}_{J'K'}$ has equivalent properties.[24,29]

We now invoke irreducible spherical tensor versions of the effective polarizability and optical activity operators (9) and (10). Since each operator in the products of the form $\hat{\alpha}^2$, $\hat{\alpha}\hat{G}$ and $\hat{\alpha}\hat{A}$ that contribute to the circular intensity sums and differences connects the same set of initial and final states $|n, JKM\rangle$ and $|n', J'K'M'\rangle$, the same spherical components must be specified in each term. The rotational angular momentum aspects of each transition tensor (i.e. the external part) is independent of the physical nature of the tensor operator, so we can write intensity factors [Eqns (19)] for each type of Raman scattering contribution:

$$[I^k_q(\alpha^2)]_{J'K',JK} = \frac{1}{2k+1}|\langle n'|\overline{\hat{\alpha}^k_{K'-K}}|n\rangle|^2 D^k_{J'K',JK} \quad (21a)$$

$$[I^k_q(\alpha G)]_{J'K',JK} = \frac{1}{2k+1}\langle n'|\overline{\hat{\alpha}^k_{K'-K}}|n\rangle\langle n'|\overline{\hat{G}^k_{K'-K}}|n\rangle^* D^k_{J'K',JK} \quad (21b)$$

Table 2. Rotational Raman factors $D^2_{J'K',JK}$

	J'		
K'	$J-2$	$J-1$	J
$K-2$	$\frac{(J+K)(J+K-1)(J+K-2)(J+K-3)}{4J(J-1)(2J+1)(2J-1)}$	$\frac{(J+K)(J+K-2)[J^2+(K-1)^2]}{2J(J+1)(J-1)(2J+1)}$	$\frac{3[J^2-(K-1)^2][(J+1)^2-(K-1)^2]}{2J(J+1)(2J-1)(2J+3)}$
$K-1$	$\frac{(J^2-K^2)(J+K-1)(J+K-2)}{J(J-1)(2J+1)(2J-1)}$	$\frac{(J+K)(J+K-1)(J-2K+1)^2}{2J(J+1)(J-1)(2J+1)}$	$\frac{3(2K-1)^2(J+K)(J-K+1)}{2J(J+1)(2J-1)(2J+3)}$
K	$\frac{3(J^2-K^2)[(J-1)^2-K^2]}{2J(J-1)(2J+1)(2J-1)}$	$\frac{3K^2(J^2-K^2)}{J(J+1)(J-1)(2J+1)}$	$\frac{[J(J+1)-3K^2]^2}{J(J+1)(2J-1)(2J+3)}$
$K+1$	$\frac{(J^2-K^2)(J-K-1)(J-K-2)}{J(J-1)(2J+1)(2J-1)}$	$\frac{(J-K)(J-K-1)(J+2K+1)^2}{2J(J+1)(J-1)(2J+1)}$	$\frac{3(2K+1)^2(J-K)(J+K+1)}{2J(J+1)(2J-1)(2J+3)}$
$K+2$	$\frac{(J-K)(J-K-1)(J-K-2)(J-K-3)}{4J(J-1)(2J+1)(2J-1)}$	$\frac{(J-K)(J-K-2)[J^2-(K+1)^2]}{2J(J+1)(J-1)(2J+1)}$	$\frac{3[J^2-(K+1)^2][(J+1)^2-(K+1)^2]}{2J(J+1)(2J-1)(2J+3)}$

	J'	
K'	$J+1$	$J+2$
$K-2$	$\frac{[(J+1)^2-(K-1)^2](J-K+1)(J-K+3)}{2J(J+1)(J+2)(2J+1)}$	$\frac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$
$K-1$	$\frac{(J+2K)^2(J-K+1)(J-K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
K	$\frac{3K^2[(J+1)^2-K^2]}{J(J+1)(J+2)(2J+1)}$	$\frac{3[(J+1)^2-K^2][(J+2)^2-K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$
$K+1$	$\frac{(J-2K)^2(J+K+1)(J+K+2)}{2J(J+1)(J+2)(2J+1)}$	$\frac{[(J+1)^2-K^2](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$
$K+2$	$\frac{[(J+1)^2-(K+1)^2](J+K+1)(J+K+3)}{2J(J+1)(J+2)(2J+1)}$	$\frac{(J+K+1)(J+K+2)(J+K+3)(J+K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$

$$[I^k_q(\alpha A)]_{J'K',JK} = \frac{1}{2k+1}\langle n'|\overline{\hat{\alpha}^k_{K'-K}}|n\rangle\langle n'|\overline{\hat{A}^k_{K'-K}}|n\rangle^* D^k_{J'K',JK} \quad (21c)$$

Selection rules for optically active scattering therefore devolve entirely upon the internal parts of the matrix elements.

It remains to convert the cartesian components of the tensors $\hat{\alpha}_{\alpha\beta}$, $\hat{G}_{\alpha\beta}$ and $\hat{A}_{\alpha\beta\gamma}$ specified in the circular intensity sums and differences [Eqns (2)] into irreducible spherical form. Second-rank sets are readily available, but appropriate third-rank sets are hard to find. Stone[33,34] has provided systematic procedures for converting between cartesian and spherical tensors, but in this instance we found it easier to generate the required third-rank sets using the following equation for constructing irreducible tensor operators from products of two arbitrary tensor operators $\hat{T}(1)^{k_1}$ and $\hat{T}(2)^{k_2}$ of rank k_1 and k_2:[35]

$$[\hat{T}(1)^{k_1}\times\hat{T}(2)^{k_2}]^k_q = \sum_{q_1q_2}(-1)^{k_1-k_2-q}(2k+1)^{1/2}\begin{pmatrix}k_1 & k_2 & k\\ q_1 & q_2 & -q\end{pmatrix}\times\hat{T}(1)^{k_1}_{q_1}\hat{T}(2)^{k_2}_{q_2} \quad (22)$$

Since

$$\mathscr{D}^1\times\mathscr{D}^1\times\mathscr{D}^1 = \mathscr{D}^0+3\mathscr{D}^1+2\mathscr{D}^2+\mathscr{D}^3 \quad (23)$$

where $\mathscr{D}^k$ is the irreducible representation of the proper rotation group of dimension k, it follows that a general third-rank tensor has 27 independent components with three degenerate first-rank and two degenerate second-rank sets. Fortunately, $\hat{A}_{\alpha\beta\gamma}$ is symmetric and traceless in its last two subscripts [from the properties of the quadrupole moment, Eqns (5)], and since a second-rank symmetric traceless tensor spans $\mathscr{D}^2$, it follows from

$$\mathscr{D}^1\times\mathscr{D}^2 = \mathscr{D}^1+\mathscr{D}^2+\mathscr{D}^3 \quad (24)$$

that $\hat{A}_{\alpha\beta\gamma}$ has just 15 independent components with no degeneracies. Thus, by taking $k_1=1$ and $k_2=2$ in Eqn (22), it is possible to obtain unique irreducible sets for $\hat{A}_{\alpha\beta\gamma}$ that can be readily interconverted between cartesian and spherical form. The required sets for $\hat{\alpha}_{\alpha\beta}$ and $\hat{A}_{\alpha\beta\gamma}$ are listed in the Appendix; we have not given the sets for $\hat{G}_{\alpha\beta}$ since these are identical in form with $\hat{\alpha}_{\alpha\beta}$ (polar and axial tensors have identical transformation properties under proper rotations). Chiu[36] listed equivalent sets, but with different constants and phase factors, which he used for a discussion of new selection rules for higher order rotational Raman scattering processes.

Symmetric top selection rules

We first apply these results to derive the selection rules for conventional pure rotational Raman scattering in

symmetric tops. This means that the initial and final internal states $|n\rangle$ and $|n'\rangle$ correspond to the molecule in its ground vibrational and electronic level; however, in order to accommodate the possibility of antisymmetric scattering we allow the electronic state to be degenerate so that $|n\rangle$ and $|n'\rangle$ could correspond to different components. Denoting the molecule-fixed principal axes by X, Y and Z, with Z as the symmetry axis, the only non-zero symmetric polarizability components are $\alpha_{ZZ} = \alpha_{\parallel}$ and $\alpha_{XX} = \alpha_{YY} = \alpha_{\perp}$ so that only the following internal symmetric irreducible spherical operator components survive:

$$\bar{\hat{\alpha}}^0_0 = -\sqrt{3}\hat{\alpha} \tag{25a}$$

$$\bar{\hat{\alpha}}^2_0 = \frac{2}{\sqrt{6}}(\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}) \tag{25b}$$

where $\alpha = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ})$ is the mean polarizability. It follows from Table 4 in Ref. 11 that the only non-zero antisymmetric polarizability component is $\alpha_{XY} = -\alpha_{YX}$; however, this is not supported by all symmetric tops, only those belonging to point groups C_3, S_6, C_4, S_4, C_{4h}, C_6, C_{3h} and C_{6h}. The corresponding internal antisymmetric irreducible spherical operator component is therefore

$$\bar{\hat{\alpha}}^1_0 = \frac{i}{\sqrt{2}}(\hat{\alpha}_{XY} - \hat{\alpha}_{YX}) \tag{26}$$

However, since the antisymmetric part [Eqn (9c)] of the effective polarizability operator is time-odd, further considerations are required in order to know if a particular molecule can support antisymmetric scattering, in particular the behaviour of the electronic state under time reversal.[11,22,37] An earlier discussion of antisymmetric rotational Raman scattering did not invoke time reversal arguments and so the conclusions are misleading.[23]

A consequence of Eqns (25) and (26) is that $K' - K = 0$ in the intensity factors [Eqns (21)]. Using the factors $D^k_{J'K',JK}$ listed in Tables 1 and 2, the non-zero intensity factors for conventional Raman scattering are found to be as follows:

(a) $\Delta J = 0$, $\Delta K = 0$:

$$[I^0_q(\alpha^2)]_{JK,JK} = 3|\langle n'|\hat{\alpha}|n\rangle|^2 \tag{27a}$$

$$[I^1_q(\alpha^2)]_{JK,JK} = \frac{2K^2}{3J(J+1)}|\langle n'|\hat{\alpha}_{XY} - \hat{\alpha}_{YX}|n\rangle|^2 \tag{27b}$$

$$[I^2_q(\alpha^2)]_{JK,JK} = \frac{2[3K^2 - J(J+1)]^2}{15J(J+1)(2J+3)(2J-1)} \times|\langle n'|\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}|n\rangle|^2 \tag{27c}$$

(b) $\Delta J = +1$, $\Delta K = 0$:

$$[I^1_q(\alpha^2)]_{J+1K,JK} = \frac{(J+K+1)(J-K+1)}{6(J+1)(2J+1)} \times|\langle n'|\hat{\alpha}_{XY} - \hat{\alpha}_{YX}|n\rangle|^2 \tag{27d}$$

$$[I^2_q(\alpha^2)]_{J+1K,JK} = \frac{2K^2(J+K+1)(J-K+1)}{5J(J+2)(J+1)(2J+1)} \times|\langle n'|\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}|n\rangle|^2 \tag{27e}$$

(c) $\Delta J = -1$, $\Delta K = 0$:

$$[I^1_q(\alpha^2)]_{J-1K,JK} = \frac{(J+K)(J-K)}{6J(2J+1)} \times|\langle n'|\hat{\alpha}_{XY} - \hat{\alpha}_{YX}|n\rangle|^2 \tag{27f}$$

$$[I^2_q(\alpha^2)]_{J-1K,JK} = \frac{2K^2(J+K)(J-K)}{5J(J+1)(2J+1)(J-1)} \times|\langle n'|\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}|n\rangle|^2 \tag{27g}$$

(d) $\Delta J = +2$, $\Delta K = 0$:

$$[I^2_q(\alpha^2)]_{J+2K,JK} = \frac{(J+K+1)(J+K+2)(J-K+1)(J-K+2)}{5(J+1)(J+2)(2J+1)(2J+3)} \times|\langle n'|\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}|n\rangle|^2 \tag{27h}$$

(e) $\Delta J = -2$, $\Delta K = 0$:

$$[I^2_q(\alpha^2)]_{J-2K,JK} = \frac{(J+K)(J+K-1)(J-K)(J-K-1)}{5J(2J+1)(J-1)(2J-1)} \times|\langle n'|\hat{\alpha}_{\parallel} - \hat{\alpha}_{\perp}|n\rangle|^2 \tag{27i}$$

Hence the well known selection rules for symmetric scattering, namely $\Delta J = 0, \pm 1, \pm 2$; $\Delta K = 0$; with $\Delta J = \pm 1$ forbidden if $K = 0$. The selection rules for antisymmetric scattering also follow immediately, namely $\Delta J = 0, \pm 1$; $\Delta K = 0$; with $\Delta J = 0$ forbidden if $K = 0$. Apart from these selection rules we see that, within the Born-Oppenheimer approximation, the generation of antisymmetric rotational Raman scattering does not depend on the nature of the rotational transition; it requires degeneracy in the electronic state. However, if the Coriolis coupling between the electronic motion and the molecular rotation is taken into account, antisymmetric scattering is possible even if the electronic state is non-degenerate.[38]

These selection rules also apply to vibration-rotation Raman scattering in fundamentals of totally symmetric modes of vibration. Selection rules for non-totally symmetric fundamentals are more complicated because additional components must be included in the polarizability operators.[23,24,28-31]

Rotational Raman optical activity

The ROA is calculated by converting the products of cartesian tensor components in the circular intensity sums and differences [Eqns (2)] into irreducible spherical operator form (using the relationships in the Appendix) and interpreting each term as a corresponding intensity factor [Eqns (21)]. The non-zero ROA contributions have the following form:

$$\tilde{\alpha}_{xx}\tilde{G}^*_{xx} \to \tfrac{1}{4}(\tfrac{4}{3}\hat{\alpha}^0_0\hat{G}^{0*}_0 + \tfrac{2}{3}\hat{\alpha}^2_0\hat{G}^{2*}_0 + \hat{\alpha}^2_2\hat{G}^{2*}_2 + \hat{\alpha}^2_{-2}\hat{G}^{2*}_{-2}) \tag{28a}$$

$$\tilde{\alpha}_{xy}\tilde{G}^*_{xy} \to \tfrac{1}{4}(2\hat{\alpha}^1_0\hat{G}^{1*}_0 + \hat{\alpha}^2_2\hat{G}^{2*}_2 + \hat{\alpha}^2_{-2}\hat{G}^{2*}_{-2}) \tag{28b}$$

$$\tilde{\alpha}_{zx}\tilde{G}^*_{zx} \to \tfrac{1}{4}(\hat{\alpha}^1_1\hat{G}^{1*}_1 + \hat{\alpha}^1_{-1}\hat{G}^{1*}_{-1} + \hat{\alpha}^2_1\hat{G}^{2*}_1 + \hat{\alpha}^2_{-1}\hat{G}^{2*}_{-1}) \tag{28c}$$

$$\tilde{\alpha}_{zy}\tilde{G}^*_{zy} \to \tfrac{1}{4}(\hat{\alpha}^1_1\hat{G}^{1*}_1 + \hat{\alpha}^1_{-1}\hat{G}^{1*}_{-1} + \hat{\alpha}^2_1\hat{G}^{2*}_1 + \hat{\alpha}^2_{-1}\hat{G}^{2*}_{-1}) \tag{28d}$$

$$\tilde{\alpha}_{xx}\tilde{A}^{*}_{xyz} \rightarrow \frac{i}{2\sqrt{6}}[\tfrac{1}{2}(\hat{\alpha}^{2}_{2}\hat{A}^{2*}_{2}+\hat{\alpha}^{2}_{-2}\hat{A}^{2*}_{-2})-\hat{\alpha}^{2}_{0}\hat{A}^{2*}_{0}] \quad (28e)$$

$$\tilde{\alpha}_{xy}\tilde{A}^{*}_{xxz} \rightarrow -\frac{i}{4\sqrt{6}}\left(\hat{\alpha}^{2}_{2}\hat{A}^{2*}_{2}+\hat{\alpha}^{2}_{-2}\hat{A}^{2*}_{-2}-\frac{6}{\sqrt{5}}\hat{\alpha}^{1}_{0}\hat{A}^{1*}_{0}\right) \quad (28f)$$

$$\tilde{\alpha}_{zx}\tilde{A}^{*}_{zzy} \rightarrow -\frac{i}{4\sqrt{6}}\left[\hat{\alpha}^{2}_{1}\hat{A}^{2*}_{1}+\hat{\alpha}^{2}_{-1}\hat{A}^{2*}_{-1} -\frac{3}{\sqrt{5}}(\hat{\alpha}^{1}_{1}\hat{A}^{1*}_{1}+\hat{\alpha}^{1}_{-1}\hat{A}^{1*}_{-1})\right] \quad (28g)$$

$$\tilde{\alpha}_{zy}\tilde{A}^{*}_{zzx} \rightarrow \frac{i}{4\sqrt{6}}\left[\hat{\alpha}^{2}_{1}\hat{A}^{2*}_{1}+\hat{\alpha}^{2*}_{-1}\hat{A}^{2*}_{-1} -\frac{3}{\sqrt{5}}(\hat{\alpha}^{1}_{1}\hat{A}^{1*}_{1}+\hat{\alpha}^{1}_{-1}\hat{A}^{1*}_{-1})\right] \quad (28h)$$

By interpreting $\hat{\alpha}^{k}_{q}\hat{G}^{k*}_{q}$ and $\hat{\alpha}^{k}_{q}\hat{A}^{k*}_{q}$ as $[I^{k}_{q}(\alpha G)]_{J'K',JK}$ and $[I^{k}_{q}(\alpha A)]_{J'K',JK}$ and neglecting the antisymmetric scattering contributions (which is always valid at transparent frequencies, irrespective of the nature of the initial and final vibrational-electronic states),[11,22] the ROA intensity factors to be used in Eqns (2) are found to be as follows:

$$\mathrm{Im}\,(\tilde{\alpha}_{xx}\tilde{G}^{*}_{xx}+\tilde{\alpha}_{xy}\tilde{G}^{*}_{xy}) \rightarrow \tfrac{1}{45}[7(\alpha_{\parallel}-\alpha_{\perp})(G'_{\parallel}-G'_{\perp})D^{2}_{J'K,JK}+45\alpha G'D^{0}_{J'K,JK}] \quad (29a)$$

$$\mathrm{Im}\,(\tilde{\alpha}_{zx}\tilde{G}^{*}_{zx}+\tilde{\alpha}_{zy}\tilde{G}^{*}_{zy}) \rightarrow \tfrac{2}{15}(\alpha_{\parallel}-\alpha_{\perp})(G'_{\parallel}-G'_{\perp})D^{2}_{J'K,JK} \quad (29b)$$

$$\tfrac{1}{3}\omega\ \mathrm{Re}\,(\tilde{\alpha}_{xx}\tilde{A}^{*}_{xyz}-\tilde{\alpha}_{xy}\tilde{A}^{*}_{xxz}) \rightarrow \tfrac{1}{90}\omega(\alpha_{\parallel}-\alpha_{\perp})(A_{XYZ}-A_{YZX})D^{2}_{J'K,JK} \quad (29c)$$

$$\tfrac{1}{3}\omega\ \mathrm{Re}\,(\tilde{\alpha}_{zx}\tilde{A}^{*}_{zzy}-\tilde{\alpha}_{zy}\tilde{A}^{*}_{zzx}) \rightarrow -\tfrac{1}{45}\omega(\alpha_{\parallel}-\alpha_{\perp})(A_{XYZ}-A_{YZX})D^{2}_{J'K,JK} \quad (29d)$$

where $G'=\frac{1}{3}(G'_{XX}+G'_{YY}+G'_{ZZ})$. Similarly, the required conventional intensity factors are

$$\tilde{\alpha}_{xx}\tilde{\alpha}^{*}_{xx}+\tilde{\alpha}_{xy}\tilde{\alpha}^{*}_{xy} \rightarrow \tfrac{1}{45}[7(\alpha_{\parallel}-\alpha_{\perp})^{2}D^{2}_{J'K,JK}+45\alpha^{2}D^{0}_{J'K,JK}] \quad (30a)$$

$$\tilde{\alpha}_{zx}\tilde{\alpha}^{*}_{zx}+\tilde{\alpha}_{zy}\tilde{\alpha}^{*}_{zy} \rightarrow \tfrac{2}{15}(\alpha_{\parallel}-\alpha_{\perp})^{2}D^{2}_{J'K,JK} \quad (30b)$$

We have specialized here to the case of pure rotational Raman scattering, so that $\alpha_{\parallel}-\alpha_{\perp}$, etc., are the corresponding tensors for the molecule in the ground vibrational-electronic state.

We can now write down the polarized and depolarized CIDs Δ_x and Δ_z [Eqn (1)] associated with the different allowed rotational Raman transitions.

(a) Rayleigh line ($\Delta J=0$, $\Delta K=0$):

For a molecule in a particular state $|JKM\rangle$:

$$\Delta_x=\frac{2}{c}\left\{45\alpha G'+\frac{[3K^{2}-J(J+1)]^{2}}{J(J+1)(2J+3)(2J-1)} \times\left[7(\alpha_{\parallel}-\alpha_{\perp})(G'_{\parallel}-G'_{\perp})+\frac{\omega}{2}(\alpha_{\parallel}-\alpha_{\perp})(A_{XYZ}-A_{YZX})\right]\right\} \times\left\{45\alpha^{2}+\frac{7[3K^{2}-J(J+1)]^{2}}{J(J+1)(2J+3)(2J-1)}(\alpha_{\parallel}-\alpha_{\perp})^{2}\right\}^{-1} \quad (31a)$$

$$\Delta_z=\frac{2[(G'_{\parallel}-G'_{\perp})-\frac{1}{6}\omega(A_{XYZ}-A_{YZX})]}{c(\alpha_{\parallel}-\alpha_{\perp})} \quad (31b)$$

Clearly, Δ_z is independent of temperature, but Δ_x, since it is a function of J and K, is temperature-dependent and a quantum statistical average should be taken. However, a useful approximate result can be obtained if $K=0$ and $J>3$, for then

$$\frac{[3K^{2}-J(J+1)]^{2}}{J(J+1)(2J+3)(2J-1)}\approx\frac{1}{4}$$

so that

$$\Delta_x \rightarrow \frac{2\{45\alpha G'+\frac{1}{4}[7(\alpha_{\parallel}-\alpha_{\perp})(G'_{\parallel}-G'_{\perp})+\frac{1}{2}\omega(\alpha_{\parallel}-\alpha_{\perp})(A_{XYZ}-A_{YZX})]\}}{c[45\alpha^{2}+\frac{7}{4}(\alpha_{\parallel}-\alpha_{\perp})^{2}]} \quad (32)$$

with increasing temperature.

(b) Raman lines ($\Delta J=\pm1,\pm2$; $\Delta K=0$):

$$\Delta_x=\frac{2[7(G'_{\parallel}-G'_{\perp})+\frac{1}{2}\omega(A_{XYZ}-A_{YZX})}{7c(\alpha_{\parallel}-\alpha_{\perp})} \quad (33a)$$

$$\Delta_z=\frac{2[(G'_{\parallel}-G'_{\perp})-\frac{1}{6}\omega(A_{XYZ}-A_{YZX})]}{c(\alpha_{\parallel}-\alpha_{\perp})} \quad (33b)$$

In the case that the separate transitions are not resolved, the total scattered intensity from the Rayleigh line and all the rotational Raman lines is measured. This means that, for each initial state $|JK\rangle$, we must sum the intensity factors over all the allowed transitions to final states $|J'K'\rangle$, and then take a quantum-statistical average of the resulting expressions over all possible initial states $|JK\rangle$ using

$$\bar{X}=\frac{\sum_j X^{(j)}\,e^{-W_j/kT}}{\sum_j e^{-W_j/kT}} \quad (34)$$

where $X^{(j)}$ is the value of the quantity X in the jth quantum state. Since $\Delta K=0$, the use of the sum rule [Eqn (20c)] gives a constant result for each intensity factor $(I^{k}_{q})_{J'K,JK}$ [Eqn (21)] when summed over all allowed final states $|J'K\rangle$ for a given initial state $|JK\rangle$, which means that when the average [Eqn (34)] over all initial states $|JK\rangle$ is taken a temperature-independent result is obtained. Specifically, the unresolved CIDs are found to be

$$\Delta_x=\frac{2[45\alpha G'+7(\alpha_{\parallel}-\alpha_{\perp})(G'_{\parallel}-G'_{\perp})+\frac{1}{2}\omega(\alpha_{\parallel}-\alpha_{\perp})(A_{XYZ}-A_{YZX})]}{c[45\alpha^{2}+7(\alpha_{\parallel}-\alpha_{\perp})^{2}]} \quad (35a)$$

and

$$\Delta_z=\frac{2[(G'_{\parallel}-G'_{\perp})-\frac{1}{6}\omega(A_{XYZ}-A_{YZX})]}{c(\alpha_{\parallel}-\alpha_{\perp})} \quad (35b)$$

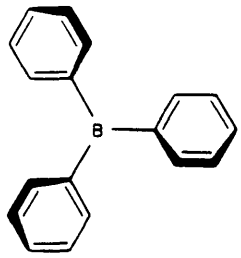
These results are precisely the CIDs [Eqns (6)] for an isotropic fluid in the case of axial symmetry[11] and so conform to the 'principle of spectroscopic stability'.[39]

Notice that the nature of the initial and final rotational quantum states does not influence the Raman optical activity. The latter is determined solely by the nature of the internal vibrational-electronic states, and so the structure must be chiral in order that the same components of polar and axial tensors such as $\alpha_{\alpha\beta}$ and $G'_{\alpha\beta}$ have the same transformation properties.[11]

DISCUSSION

In molecules sufficiently large to be chiral, it is unlikely that the separate rotational Raman transitions would be resolved. However, the separate transitions all show the same CIDs [Eqns (33)], so it is sufficient that the envelope of unresolved rotational Raman bands be resolved from the central sharp Rayleigh line, since this has a different polarized CID [Eqn (31a)], although the depolarized CID [Eqn (31b)] is the same. Thus if the polarizability anisotropy $(\alpha_\parallel - \alpha_\perp)$ were known from other measurements (such as depolarization ratio or Kerr effect), it would be possible to extract from the polarized and depolarized CIDs of the unresolved rotational Raman bands values for the two optical activity anisotropies $(G'_\parallel - G'_\perp)$ and $(A_{XYZ} - A_{YZX})$.

Chiral symmetric top molecules belong to point groups C_n or D_n with $n > 2$. An example with D_3 symmetry is triphenylborane shown below. The minimum



energy conformations of this molecule are known to be chiral, with the aromatic rings constituting a left- or right-handed propeller (that shown above is left-handed), but unfortunately they are unresolvable.[40] Nonetheless, it provides an instructive example for an explicit calculation of rotational Raman optical activity. This is performed in the Appendix using a group polarizability model in which the optical activity effects originate in the origin-dependence of the tensors $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$.

Unfortunately, examples of chiral symmetric top molecules that are sufficiently simple for useful rotational Raman features to be observable are hard to find. Any chiral molecule sufficiently small and volatile is likely to be an asymmetric top. Asymmetric top wavefunctions depend only on the quantum numbers J and M and so have definite parity. They are usually written as linear combinations of definite parity pairs of symmetric top functions ($|JKM\rangle$ alone has mixed parity),[27,41] and so intensity factors corresponding to transitions between asymmetric top states reduce to weighted sums of intensity factors between symmetric top states. However, because the principal inertial and principal polarizability axes no longer coincide in most chiral asymmetric tops, transitions with $\Delta K = \pm 1, \pm 2$ are now allowed in addition to those with $\Delta K = 0$, which are the only ones allowed in a symmetric top. Hence the theory of rotational ROA in a general chiral asymmetric top is much more complicated, and is deferred to a later paper along with discussion of rotation-vibration ROA.

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APPENDIX

Irreducible sets of tensor components required in the text

It is important to realize that the usual statement of the Condon and Shortley phase convention

$$Y^l_{-m} = (-1)^m Y^{l*}_m$$

applies only to the spherical harmonics Y^l_m. For general spherical tensor components the corresponding statement is

$$T^l_{-m} = (-1)^{n+l-m} T^{l*}_m$$

where n is the rank of the associated cartesian tensor, which follows from Eqns (1.2) and (2.1) in Stone's paper.[33] As well as the required third-rank sets, we have also given the corresponding first- and second-rank sets for completeness, even though these are completely standard.

(a) First-rank tensor, exemplified by the electric dipole moment operator. Only one set, spanning $\mathcal{D}^1$, can be constructed.

$$\mu^1_1 = -\frac{1}{\sqrt{2}}(\mu_x + i\mu_y)$$

$$\mu^1_0 = \mu_z$$

$$\mu^1_{-1} = \frac{1}{\sqrt{2}}(\mu_x - i\mu_y)$$

The inverse relationships are

$$\mu_x = -\frac{1}{\sqrt{2}}(\mu^1_1 - \mu^1_{-1})$$

$$\mu_y = \frac{i}{\sqrt{2}}(\mu^1_1 + \mu^1_{-1})$$

$$\mu_z = \mu^1_0$$

(b) Second-rank tensor, exemplified by the effective polarizability operator $\alpha_{\alpha\beta}$. The effective electric dipole-magnetic dipole optical activity operator $G_{\alpha\beta}$ has the same form. Three sets can be constructed, spanning $\mathcal{D}^0$, $\mathcal{D}^1$ and $\mathcal{D}^2$.

$$\alpha^0_0 = -\frac{1}{\sqrt{3}}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\alpha^1_1 = -\frac{1}{2}[\alpha_{xz} - \alpha_{zx} + i(\alpha_{yz} - \alpha_{zy})]$$

$$\alpha^1_0 = \frac{i}{\sqrt{2}}(\alpha_{xy} - \alpha_{yx})$$

$$\alpha^1_{-1} = -\frac{1}{2}[\alpha_{xz} - \alpha_{zx} - i(\alpha_{yz} - \alpha_{zy})]$$

$$\alpha^2_2 = \frac{1}{2}[\alpha_{xx} - \alpha_{yy} + i(\alpha_{yx} + \alpha_{xy})]$$

$$\alpha^2_1 = -\frac{1}{2}[\alpha_{xz} + \alpha_{zx} + i(\alpha_{yz} + \alpha_{zy})]$$

$$\alpha^2_0 = \frac{1}{\sqrt{6}}[2\alpha_{zz} - (\alpha_{xx} + \alpha_{yy})]$$

$$\alpha^2_{-1} = \frac{1}{2}[\alpha_{xz} + \alpha_{zx} - i(\alpha_{yz} + \alpha_{zy})]$$

$$\alpha^2_{-2} = \frac{1}{2}[\alpha_{xx} - \alpha_{yy} - i(\alpha_{yx} + \alpha_{xy})]$$

The inverse relationships are as follows:

$$\alpha_{xx} = \frac{1}{2}\left[-\sqrt{\frac{2}{3}}(\alpha^2_0 + \sqrt{2}\alpha^0_0) + (\alpha^2_2 + \alpha^2_{-2})\right]$$

$$\alpha_{yy} = -\frac{1}{2}\left[\sqrt{\frac{2}{3}}(\alpha^2_0 + \sqrt{2}\alpha^0_0) + (\alpha^2_2 + \alpha^2_{-2})\right]$$

$$\alpha_{zz} = \sqrt{\frac{2}{3}}\left(\alpha^2_0 - \frac{1}{\sqrt{2}}\alpha^0_0\right)$$

$$\alpha_{xy} = -\frac{i}{2}[\sqrt{2}\alpha^1_0 + (\alpha^2_2 - \alpha^2_{-2})]$$

$$\alpha_{xz} = -\frac{1}{2}[(\alpha^2_1 - \alpha^2_{-1}) + (\alpha^1_1 + \alpha^1_{-1})]$$

$$\alpha_{yx} = \frac{i}{2}[\sqrt{2}\alpha^1_0 - (\alpha^2_2 - \alpha^2_{-2})]$$

$$\alpha_{yz} = \frac{i}{2}[(\alpha^2_1 + \alpha^2_{-1}) + (\alpha^1_1 - \alpha^1_{-1})]$$

$$\alpha_{zx} = -\frac{1}{2}[(\alpha^2_1 - \alpha^2_{-1}) - (\alpha^1_1 + \alpha^1_{-1})]$$

$$\alpha_{zy} = \frac{i}{2}[(\alpha^2_1 + \alpha^2_{-1}) - (\alpha^1_1 - \alpha^1_{-1})]$$

(c) Third-rank tensor, exemplified by the effective electric dipole-electric quadrupole operator $A_{\alpha\beta\gamma}$. For a general third-rank tensor, seven sets can be constructed corresponding to $\mathcal{D}^0$, $3\mathcal{D}^1$, $2\mathcal{D}^2$ and $\mathcal{D}^3$, but since $A_{\alpha\beta\gamma}$ is symmetric and traceless in the last two subscripts, the degeneracies in $\mathcal{D}^1$ and $\mathcal{D}^2$ are removed and $\mathcal{D}^0$ vanishes.

$$A^1_1 = \sqrt{\frac{3}{10}}[A_{xxx} + A_{yyx} + A_{zzx} + i(A_{yyy} + A_{xxy} + A_{zzy})]$$

$$A^1_0 = \sqrt{\frac{3}{5}}(A_{zxx} - A_{xxz} + A_{zyy} - A_{yyz})$$

$$A^1_{-1} = -\sqrt{\frac{3}{10}}[A_{xxx} + A_{yyx} + A_{zzx} - i(A_{yyy} + A_{xxy} + A_{zzy})]$$

$$A^2_2 = \frac{1}{\sqrt{6}}[A_{xxz} - A_{zxx} + A_{zyy} - A_{yyz} - i(2A_{zxy} - A_{xyz} - A_{yzx})]$$

$$A^2_1 = \frac{1}{\sqrt{6}}[A_{xxx} + A_{zzx} + 2A_{xyy} - A_{yyx} + i(A_{yyy} + A_{zzy} + 2A_{yxx} - A_{xxy})]$$

$$A^2_0 = i(A_{xyz} - A_{yzx})$$

$$A^2_{-1} = \frac{1}{\sqrt{6}}[A_{xxx} + A_{zzx} + 2A_{xyy} - A_{yyx} - i(A_{yyy} + A_{zzy} + 2A_{yxx} - A_{xxy})]$$

$$A^2_{-2} = -\frac{1}{\sqrt{6}}[A_{xxz} - A_{zxx} + A_{zyy} - A_{yyz} + i(2A_{zxy} - A_{xyz} - A_{yzx})]$$

$$A^3_3 = \frac{1}{2\sqrt{2}}[2A_{yyx} + A_{xyy} - A_{xxx} - i(2A_{xxy} + A_{yxx} - A_{yyy})]$$

$$A^3_2 = \frac{1}{2\sqrt{3}}[2A_{xxz} + A_{zxx} - 2A_{yyz} - A_{zyy} + 2i(A_{xyz} + A_{yzx} + A_{zxy})]$$

$$A^3_1 = \frac{1}{2\sqrt{30}}[7A_{xxx} + 5A_{xyy} + 2A_{yyx} - 8A_{zzx} + i(7A_{yyy} + 5A_{yxx} + 2A_{xxy} - 8A_{zzy})]$$

$$A^3_0 = -\frac{1}{\sqrt{10}}(3A_{zxx} + 2A_{xxz} + 3A_{zyy} + 2A_{yyz})$$

$$A^3_{-1} = -\frac{1}{2\sqrt{30}}[7A_{xxx} + 5A_{xyy} + 2A_{yyx} - 8A_{zzx} - i(7A_{yyy} + 5A_{yxx} + 2A_{xxy} - 8A_{zzy})]$$

$$A^3_{-2} = \frac{1}{2\sqrt{3}}[2A_{xxz} + A_{zxx} - 2A_{yyz} - A_{zyy} - 2i(A_{xyz} + A_{yzx} + A_{zxy})]$$

$$A^3_{-3} = -\frac{1}{2\sqrt{2}}[2A_{yyx} + A_{xyy} - A_{xxx} + i(2A_{xxy} + A_{yxx} - A_{yyy})]$$

The inverse relationships, specifying only the 15 independent cartesian components, are as follows:

$$A_{xxx} = \sqrt{\frac{2}{15}}(A^1_1 - A^1_{-1}) + \frac{1}{2}\sqrt{\frac{3}{10}}(A^3_1 - A^3_{-1}) - \frac{1}{2\sqrt{2}}(A^3_3 - A^3_{-3})$$

$$A_{yyy} = -i\left[\sqrt{\frac{2}{15}}(A^1_1 + A^1_{-1}) + \frac{1}{2}\sqrt{\frac{3}{10}}(A^3_1 + A^3_{-1}) + \frac{1}{2\sqrt{2}}(A^3_3 + A^3_{-3})\right]$$

$$A_{yyx} = \frac{1}{2\sqrt{2}}\left[\sqrt{\frac{3}{5}}(A^1_1 - A^1_{-1}) - \frac{1}{\sqrt{3}}(A^2_1 + A^2_{-1}) + \frac{1}{\sqrt{15}}(A^3_1 - A^3_{-1}) + (A^3_3 - A^3_{-3})\right]$$

$$A_{xxy} = -\frac{i}{2\sqrt{2}}\left[\sqrt{\frac{3}{5}}(A_1^1+A_{-1}^1)-\frac{1}{\sqrt{3}}(A_1^2-A_{-1}^2)\right.$$
$$\left.+\frac{1}{\sqrt{15}}(A_1^3+A_{-1}^3)-(A_3^3+A_{-3}^3)\right]$$

$$A_{xyy} = \frac{1}{\sqrt{2}}\left[-\frac{1}{\sqrt{15}}(A_1^1-A_{-1}^1)+\frac{1}{\sqrt{3}}(A_1^2+A_{-1}^2)\right.$$
$$\left.+\frac{1}{2\sqrt{15}}(A_1^3-A_{-1}^3)+\frac{1}{2}(A_3^3-A_{-3}^3)\right]$$

$$A_{yxx} = \frac{i}{\sqrt{2}}\left[\frac{1}{\sqrt{15}}(A_1^1+A_{-1}^1)-\frac{1}{\sqrt{3}}(A_1^2-A_{-1}^2)\right.$$
$$\left.-\frac{1}{2\sqrt{15}}(A_1^3+A_{-1}^3)+\frac{1}{2}(A_3^3+A_{-3}^3)\right]$$

$$A_{zzx} = \frac{1}{\sqrt{2}}\left[\sqrt{\frac{3}{20}}(A_1^1-A_{-1}^1)+\frac{1}{\sqrt{12}}(A_1^2+A_{-1}^2)\right.$$
$$\left.-\frac{2}{\sqrt{15}}(A_1^3-A_{-1}^3)\right]$$

$$A_{zzy} = \frac{i}{\sqrt{2}}\left[-\sqrt{\frac{3}{20}}(A_1^1+A_{-1}^1)-\frac{1}{\sqrt{12}}(A_1^2-A_{-1}^2)\right.$$
$$\left.+\frac{2}{\sqrt{15}}(A_1^3+A_{-1}^3)\right]$$

$$A_{xxz} = \frac{1}{2}\left[-\sqrt{\frac{3}{5}}A_0^1-\sqrt{\frac{2}{5}}A_0^3+\frac{1}{\sqrt{6}}(A_2^2-A_{-2}^2)\right.$$
$$\left.+\frac{1}{\sqrt{3}}(A_2^3+A_{-2}^3)\right]$$

$$A_{yyz} = -\frac{1}{2}\left[\sqrt{\frac{3}{5}}A_0^1+\sqrt{\frac{2}{5}}A_0^3+\frac{1}{\sqrt{6}}(A_2^2-A_{-2}^2)\right.$$
$$\left.+\frac{1}{\sqrt{3}}(A_2^3+A_{-2}^3)\right]$$

$$A_{zxx} = \frac{1}{2}\left[\frac{2}{\sqrt{15}}A_0^1-\sqrt{\frac{2}{5}}A_0^3-\sqrt{\frac{2}{3}}(A_2^2-A_{-2}^2)\right.$$
$$\left.+\frac{1}{\sqrt{3}}(A_2^3+A_{-2}^3)\right]$$

$$A_{zyy} = \frac{1}{2}\left[\frac{2}{\sqrt{15}}A_0^1-\sqrt{\frac{2}{5}}A_0^3+\sqrt{\frac{2}{3}}(A_2^2-A_{-2}^2)\right.$$
$$\left.-\frac{1}{\sqrt{3}}(A_2^3+A_{-2}^3)\right]$$

$$A_{xyz} = -\frac{i}{2}\left[A_0^2+\frac{1}{\sqrt{6}}(A_2^2+A_{-2}^2)+\frac{1}{\sqrt{3}}(A_2^3-A_{-2}^3)\right]$$

$$A_{zxy} = \frac{i}{2\sqrt{3}}[\sqrt{2}\,(A_2^2+A_{-2}^2)-(A_2^3-A_{-2}^3)]$$

$$A_{yzx} = \frac{i}{2}\left[A_0^2-\frac{1}{\sqrt{6}}(A_2^2+A_{-2}^2)-\frac{1}{\sqrt{3}}(A_2^3-A_{-2}^3)\right]$$

The remaining cartesian components can be obtained from $A_{\alpha\beta\gamma} = A_{\alpha\gamma\beta}$ and $A_{\alpha\beta\beta} = 0$.

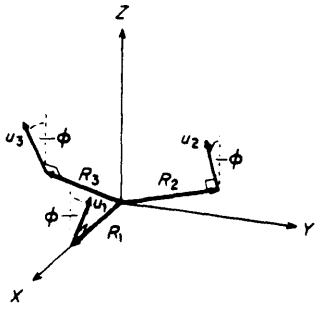

Figure 2. The geometry of triphenylborane in a left-handed propellor conformation. u_1, u_2 and u_3 are unit vectors along the effective six-fold symmetry axes of the aromatic rings.

Rotational Raman optical activity of triphenylborane

We use a group polarizability model in which the polarizability and optical activity tensors of the molecule are written as sums over a convenient set of local bond or group tensors, taking care to include the origin-dependent parts of $G'_{\alpha\beta}$ and $A_{\alpha\beta\gamma}$:[11]

$$\alpha_{\alpha\beta} = \sum_i \alpha_{i_{\alpha\beta}}$$
$$G'_{\alpha\beta} = \sum_i (G'_{i_{\alpha\beta}} - \tfrac{1}{2}\omega\varepsilon_{\beta\gamma\delta}R_{i_\gamma}\alpha_{i_{\alpha\delta}})$$
$$A_{\alpha\beta\gamma} = \sum_i [A_{i_{\alpha\beta\gamma}} + \tfrac{3}{2}(R_{i_\beta}\alpha_{i_{\alpha\gamma}} + R_{i_\gamma}\alpha_{i_{\alpha\beta}} - R_{i_\delta}\alpha_{i_{\alpha\delta}}\delta_{\beta\gamma})]$$

where $\alpha_{i_{\alpha\beta}}$, $G'_{i_{\alpha\beta}}$ and $A_{i_{\alpha\beta\gamma}}$ are the tensors pertaining to group i and referred to a local origin on i, and $\boldsymbol{R}_i$ is the vector from the molecular origin to the local group origin. Here we take the set of groups i to be the three aromatic rings, neglecting for simplicity the three B–C bonds (which contribute only to the Raman intensity, not the optical activity). Figure 2 shows the geometry of a chiral conformation of the triphenylborane molecule in which the three aromatic rings constitute the blades of a left-handed propellor. The aromatic rings are assumed to retain the same symmetry as free benzene, so that each has a six-fold symmetry axis perpendicular to the plane: this enables us to drop the intrinsic optical activity tensors $G'_{i_{\alpha\beta}}$ and $A_{i_{\alpha\beta\gamma}}$ of each aromatic ring, and to write each polarizability tensor in the form[11]

$$\alpha_{i_{\alpha\beta}} = \alpha_i(1-\kappa_i)\delta_{\alpha\beta} + 3\alpha_i\kappa_i u_{i_\alpha}u_{i_\beta}$$

where $\boldsymbol{u}_i$ is a unit vector along the principal symmetry axis and

$$\kappa = (\alpha_\parallel - \alpha_\perp)/3\alpha$$

is a dimensionless polarizability anisotropy. The molecule-fixed axes X, Y, Z are taken to coincide with the principal inertial axes with origin at the centre of mass. Each group unit vector $\boldsymbol{u}_i$ makes an angle ϕ with the Z axis. Labelling the three groups 1, 2 and 3, we have

$$R_{1_\alpha} = RI_\alpha$$
$$R_{2_\alpha} = R\left(-\frac{1}{2}I_\alpha + \frac{\sqrt{3}}{2}J_\alpha\right)$$
$$R_{3_\alpha} = -R\left(\frac{1}{2}I_\alpha + \frac{\sqrt{3}}{2}J_\alpha\right)$$
$$u_{1_\alpha} = J_\alpha \sin\phi + K_\alpha \cos\phi$$

$$u_{2_\alpha} = -\frac{\sqrt{3}}{2} I_\alpha \sin\phi - \frac{1}{2} J_\alpha \sin\phi + K_\alpha \cos\phi$$

$$u_{3_\alpha} = \frac{\sqrt{3}}{2} I_\alpha \sin\phi - \frac{1}{2} J_\alpha \sin\phi + K_\alpha \cos\phi$$

where $\boldsymbol{I}, \boldsymbol{J}, \boldsymbol{K}$ are unit vectors along X, Y, Z and $R = |\boldsymbol{R}_i|$ is the distance from the centre of each aromatic ring to the molecular centre of mass.

We now obtain

$$\alpha_\parallel - \alpha_\perp = \sum_i (\alpha_{i_{ZZ}} - \alpha_{i_{XX}})$$

$$= \tfrac{9}{4}\alpha_i \kappa_i (3\cos 2\phi + 1)$$

$$G'_\parallel - G'_\perp = \sum_i (G'_{i_{ZZ}} - G'_{i_{XX}})$$

$$= -\tfrac{27}{8}\omega R \alpha_i \kappa_i \sin 2\phi$$

$$A_{XYZ} - A_{YXZ} = \sum_i (A_{i_{XYZ}} - A_{i_{YZX}})$$

$$= -\tfrac{27}{4} R \alpha_i \kappa_i \sin 2\phi$$

$$\alpha = \tfrac{1}{3}\alpha_{\alpha\alpha} = 3\alpha_i$$

$$G' = \tfrac{1}{3} G'_{\alpha\alpha} = 0$$

Using these results in the CIDs [Eqns (33)] for the rotational Raman lines, we obtain

$$\Delta_x = -\frac{48\pi R \sin 2\phi}{7\lambda(3\cos 2\phi + 1)}$$

$$\Delta_z = -\frac{4\pi R \sin 2\phi}{\lambda(3\cos 2\phi + 1)}$$

This expression for Δ_z also applies to the Rayleigh line and to the unresolved band, but the corresponding polarized CIDs are, from Eqns (32) and (35a),

$$\Delta_x \approx -\frac{48\pi R \kappa_i^2 (3\cos 2\phi + 1)\sin 2\phi}{\lambda[320 + 7\kappa_i^2(3\cos 2\phi + 1)^2]}$$

and

$$\Delta_x = -\frac{48\pi R \kappa_i^2 (3\cos 2\phi + 1)\sin 2\phi}{\lambda[80 + 7\kappa_i^2(3\cos 2\phi + 1)^2]}$$

To estimate the magnitudes, we use the following values: $|\kappa_i| = 0.18$ (from light-scattering data on benzene);[42] $R = 0.3$ nm and $\phi = 30°$ (from x-ray data);[43] $\lambda = 500$ nm. This gives $\Delta_x = -4.48 \times 10^{-3}$ and $\Delta_z = -2.61 \times 10^{-3}$ for the Raman lines, $\Delta_x \approx -1.97 \times 10^{-5}$ and $\Delta_z = -2.61 \times 10^{-3}$ for the Rayleigh line and $\Delta_x = -7.80 \times 10^{-5}$ and $\Delta_z = -2.61 \times 10^{-3}$ for the unresolved band. Triphenylborane is actually a very favourable example: more typical values might be an order of magnitude smaller. However, most of these parameters should still be measurable, since scanning ROA instruments can detect Δ values down to *ca* 10^{-4} and optical multi-channel instruments down to *ca* 10^{-5}.[7,8]

REFERENCES

1. L. A. Nafie and M. Diem, *Acc. Chem. Res.* **12**, 296 (1979).
2. P. J. Stephens and R. Clark, in *Optical Activity and Chiral Discrimination*, edited by S. F. Mason, p. 263. Reidel, Dortmund (1979).
3. L. A. Nafie, in *Vibrational Spectra and Structure*, edited by J. R. Durig, Vol. 10, p. 153. Elsevier, Amsterdam (1981).
4. T. A. Keiderling, *Appl. Spectrosc. Rev.* **17**, 189 (1981).
5. L. D. Barron, in *Optical Activity and Chiral Discrimination*, edited by S. F. Mason, p. 219. Reidel, Dortmund (1979).
6. L. D. Barron, *Acc. Chem. Res.* **13**, 90 (1980).
7. W. Hug, in *Raman Spectroscopy*, edited by J. Lascombe and P. V. Huong, p. 3. Wiley–Heyden, Chichester (1982).
8. L. D. Barron and J. Vrbancich, *Top. Curr. Chem.* **123**, 151 (1984).
9. P. L. Polavarapu and D. F. Michalska, *J. Am. Chem. Soc.* **105**, 6190 (1983).
10. P. L. Polavarapu, *Appl. Spectrosc.* **38**, 26 (1984).
11. L. D. Barron, *Molecular Light Scattering and Optical Activity*. Cambridge University Press, Cambridge (1982).
12. Y. N. Chiu, *J. Chem. Phys.* **52**, 1042 (1970).
13. P. W. Atkins and J. A. N. F. Gomes, *Chem. Phys. Lett.* **39**, 519 (1976).
14. P. W. Atkins, *Chem. Phys. Lett.* **74**, 358 (1980).
15. L. D. Barron, *Chem. Phys. Lett.* **79**, 392 (1981).
16. L. D. Barron, *Mol. Phys.* **43**, 1395 (1981).
17. L. D. Barron and J. F. Torrance, *Chem. Phys. Lett.* **102**, 285 (1983).
18. L. A. Nafie, *Chem. Phys. Lett.* **102**, 287 (1983).
19. L. D. Barron and A. D. Buckingham, *Mol. Phys.* **20**, 1111 (1971).
20. A. D. Buckingham and R. E. Raab, *Proc. R. Soc., London, Ser. A* **345**, 365 (1975).
21. A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
22. L. D. Barron and E. Nørby-Svendsen, in *Advances in Infrared and Raman Spectroscopy*, edited by R. J. H. Clark and R. E. Hester, Vol. 8, p. 322. Heyden, London (1981).
23. J. A. Koningstein, *Introduction to the Theory of the Raman Effect*. Reidel, Dortmund (1972).
24. G. Placzek, in *Handbuch der Radiologie*, edited by E. Marx, Vol. 6, Part 2, p. 205. Akademische Verlagsgesellschaft (1934).
25. V. B. Berestetskii, E. M. Lifshitz and L. P. Pitaevskii, *Relativistic Quantum Theory, Part 1*. Pergamon Press, Oxford (1971) (but ot the 2nd ed., now called *Quantum Electrodynamics*).
26. L. D. Landau and E. M. Lifshitz, *Quantum Mechanics*, 3rd ed. Pergamon Press, Oxford (1977) (but not the earlier editions).
27. D. Papoušek and M. R. Aliev, *Molecular Vibrational–Rotational Spectra*. Elsevier, Amsterdam (1982).
28. K. Altmann and G. Strey, *J. Mol. Spectrosc.* **44**, 571 (1972).
29. G. Placzek and E. Teller, *Z. Phys.* **81**, 209 (1933).
30. S. Bhagavantam, *Scattering of Light and the Raman Effect*. Chemical Publishing Company (1942).
31. A. Weber, in *The Raman Effect*, edited by A. Anderson, Vol. 2, p. 543. Marcel Dekker, New York (1973).
32. A. R. Edmonds, *Angular Momentum in Quantum Mechanics*. Princeton University Press, Princeton, NJ (1960).
33. A. J. Stone, *Mol. Phys.* **29**, 1461 (1975).
34. A. J. Stone, *J. Phys. A* **19**, 485 (1976).
35. B. L. Silver, *Irreducible Tensor Methods*. Academic Press, New York, London (1976).
36. Y. N. Chiu, *J. Chem. Phys.* **52**, 4950 (1970).
37. C. D. Churcher and G. E. Stedman, *J. Phys. C* **14**, 2237 (1981).
38. N. B. Baranova and B. Ya. Zel'dovich, *J. Raman Spectrosc.* **7**, 118 (1978).
39. J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*. Oxford University Press, London (1932).
40. K. Mislow, *Acc. Chem. Res.* **9**, 26 (1975).
41. H. W. Kroto, *Molecular Rotation Spectra*. Wiley, Chichester (1975).
42. N. J. Bridge and A. D. Buckingham, *Proc. R. Soc., London, Ser. A* **295**, 334 (1966).
43. F. Zettler, A. D. Hausen and H. Hess, *J. Organomet. Chem.* **72**, 157 (1974).

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Discrimination in the dispersion interaction between odd-electron chiral molecules

by L. D. BARRON and C. J. JOHNSTON
Chemistry Department, The University, Glasgow G12 8QQ, Scotland

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The time-odd part of the molecular optical activity tensor is shown to provide new contributions to the discriminating dispersion interaction between chiral molecules in degenerate states. Detailed calculations on a hypothetical odd-electron chiral transition metal complex of O^* symmetry indicate that the new discriminating contributions could be within an order of magnitude of the conventional discriminating contributions. In the near zone, the new contributions have the usual R^{-6} dependence, but in the wave zone they depend on R^{-7}, unlike the conventional discriminating contributions which depend on R^{-9}.

1. Introduction

Among the unique properties of chiral molecules are their discriminatory interactions [1]. In particular, the difference in the interaction energy between pairs of chiral molecules with the same absolute configuration and pairs with opposite absolute configurations has attracted much attention recently [1–5]. Although chiral discrimination in the dispersion interaction is expected to be weaker than in other interactions such as 'contact', electrostatic and hydrogen bonding, it is universal. The purpose of this article is to discuss additional contributions to the discriminating dispersion interactions between chiral molecules in degenerate states, particularly Kramers degeneracy associated with an odd number of electrons.

Molecules in degenerate quantum states can support, in addition to the usual range of time-even property tensors, time-odd property tensors that generate new phenomena [6–8]. Although phenomena that are linear in time-odd property tensors, such as the Faraday effect, are only manifest in the presence of some time-odd influence such as a magnetic field, phenomena that are quadratic in such tensors do not require a time-odd influence. Antisymmetric light scattering provides a good example [6–10]. Buckingham and Joslin [11] have discussed spin-dependent dispersion forces between alkali metal atoms which originate in the same property and transition tensors as antisymmetric scattering, namely the time-odd parts of the polarizability. Although the existence of analogous contributions to discriminating dispersion interactions between odd-electron chiral molecules originating in the time-odd parts of the optical activity tensors was mooted several years ago [12, 7], the detailed theory has not been developed previously.

2. The near-zone limit: single-centre formalism

The near-zone limit refers to separations R of the interacting pair that are much smaller than the wavelengths characteristic of the molecular electronic transitions so

that retardation effects can be neglected in the calculation of dispersion interactions [5]. This situation is conventionally treated using second-order perturbation theory [13].

The wavefunctions are written as simple products $|n_1 n_2\rangle$ of the separate wavefunctions $|n_1\rangle$ and $|n_2\rangle$ of molecules 1 and 2. The perturbation hamiltonian is taken to be the operator equivalent of the dipole–dipole interaction energy for two neutral charge and current distributions [13, 7]

$$V = \frac{1}{4\pi\varepsilon_0}(-T_{\alpha\beta}\mu_{1_\alpha}\mu_{2_\beta} + \ldots) + \frac{\mu_0}{4\pi}(-T_{\alpha\beta}m_{1_\alpha}m_{2_\beta} + \ldots), \tag{2.1}$$

where

$$\mu_\alpha = \sum_i e_i r_{i_\alpha}, \tag{2.2a}$$

$$m_\alpha = \sum_i \frac{e_i}{2m_i}(l_{i_\alpha} + g_i s_{i_\alpha}), \tag{2.2b}$$

are the electric and magnetic dipole moments for the collection of charges e_i with mass m_i and orbital and spin angular momenta $\mathbf{l}_i$ and $\mathbf{s}_i$ and g-factor g_i, and

$$T_{\alpha\beta} = T_{\beta\alpha} = \nabla_\alpha\nabla_\beta R^{-1} = (3R_\alpha R_\beta - R^2\delta_{\alpha\beta})R^{-5}, \tag{2.2c}$$

where $\mathbf{R} = \mathbf{R}_2 - \mathbf{R}_1$ is the vector from the origin on molecule 1 to that on 2. The dipole dispersion energy is then [13]

$$U = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 T_{\alpha\beta}T_{\gamma\delta}\sum_{\substack{j_1\neq n_1\\ j_2\neq n_2}}\frac{\langle n_1 n_2|\mu_{1_\alpha}\mu_{2_\beta}|j_1 j_2\rangle\langle j_1 j_2|\mu_{1_\gamma}\mu_{2_\delta}|n_1 n_2\rangle}{\hbar(\omega_{j_1 n_1} + \omega_{j_2 n_2})}. \tag{2.3}$$

It is well-known that, using the identities

$$\frac{1}{A+B} = \frac{2}{\pi}\int_0^\infty \frac{AB}{(A^2+u^2)(B^2+u^2)}\,du = \frac{2}{\pi}\int_0^\infty \frac{u^2}{(A^2+u^2)(B^2+u^2)}\,du, \tag{2.4}$$

with $A > 0$, $B > 0$, the dispersion energy (2.3) can be separated into single-centre contributions involving the individual molecular *dynamic* polarizability tensors at imaginary frequencies [13]

$$U = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2\left(\frac{\hbar}{2\pi}\right)T_{\alpha\beta}T_{\gamma\delta}\int_0^\infty [\alpha_{1_{\alpha\gamma}}(iu)\alpha_{2_{\beta\delta}}(iu) + \alpha'_{1_{\alpha\gamma}}(iu)\alpha'_{2_{\beta\delta}}(iu)]\,du, \tag{2.5}$$

where [13, 7]

$$\alpha_{\alpha\beta}(\omega) = \frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2 - \omega^2}\,\mathrm{Re}\,(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) = \alpha_{\beta\alpha}(\omega), \tag{2.6a}$$

$$\alpha'_{\alpha\beta}(\omega) = -\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2 - \omega^2}\,\mathrm{Im}\,(\langle n|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle) = -\alpha'_{\beta\alpha}(\omega), \tag{2.6b}$$

with $\omega = iu$.

Interference between the electric and magnetic dipole–dipole interaction operators generates the following contribution to the discriminating dispersion inter-

action between two chiral molecules [14, 15, 5]

$$U' = -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)T_{\alpha\beta}\,T_{\gamma\delta}\sum_{\substack{j_1\neq n_1\\ j_2\neq n_2}}\left\{\frac{1}{\hbar(\omega_{j_1n_1}+\omega_{j_2n_2})}\right.$$
$$\times\left(\langle n_1 n_2|\mu_{1_\alpha}\mu_{2_\beta}|j_1 j_2\rangle\langle j_1 j_2|m_{1_\gamma}m_{2_\delta}|n_1 n_2\rangle\right.$$
$$\left.\left.+\,\langle n_1 n_2|m_{1_\alpha}m_{2_\beta}|j_1 j_2\rangle\langle j_1 j_2|\mu_{1_\gamma}\mu_{2_\delta}|n_1 n_2\rangle\right)\right\}. \tag{2.7}$$

Again using the identities (2.4), this can be separated into single-centre contributions

$$U' = -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar}{\pi}\right)T_{\alpha\beta}\,T_{\gamma\delta}\int_0^\infty\left[G_{1_{\alpha\gamma}}(iu)G_{2_{\beta\delta}}(iu)+G'_{1_{\alpha\gamma}}(iu)G'_{2_{\beta\delta}}(iu)\right]du, \tag{2.8}$$

where

$$G_{\alpha\beta}(\omega)=\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega_{jn}}{\omega_{jn}^2-\omega^2}\,\mathrm{Re}\,(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle), \tag{2.9a}$$

$$G'_{\alpha\beta}(\omega)=-\frac{2}{\hbar}\sum_{j\neq n}\frac{\omega}{\omega_{jn}^2-\omega^2}\,\mathrm{Im}\,(\langle n|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle) \tag{2.9b}$$

are the optical activity tensors [13, 7].

We now consider the encounter of two molecules, each with an odd number of electrons. For simplicity we shall consider only the case of a twofold Kramers degeneracy with effective spin states $|S, M_s\rangle = |\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle$, $\alpha = |\tfrac{1}{2}, \tfrac{1}{2}\rangle$ and $\beta = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$ being the conventional shorthand. Although the electronic wavefunctions are not usually antisymmetrized since the indistinguishability of electrons plays little rôle in determining intermolecular interactions at the separations we are considering, antisymmetrization is essential for any discussion of spin-dependent features. Thus in the absence of a magnetic field, and neglecting exchange interactions, there are four degenerate zeroth-order eigenfunctions: a singlet and three triplets. As we shall see, the dispersion interaction will lift some of this degeneracy. Assuming $C_{\infty v}$ symmetry for the interacting pair, which obtains for two unlike atoms or two unlike molecules which have effectively spherical symmetry (e.g. belonging to cubic point groups), the singlet transforms as Σ^+ and the triplets as Σ^- and $\Pi_{\pm 1}$. In terms of one-electron spin states quantized along the intermolecular axis, the singlet state is

$$|\Sigma^+\rangle=\frac{1}{\sqrt{2}}(|\alpha_1\beta_2\rangle-|\beta_1\alpha_2\rangle), \tag{2.10a}$$

and the three triplet states are

$$|\Pi_{+1}\rangle=|\alpha_1\alpha_2\rangle, \tag{2.10b}$$

$$|\Sigma^-\rangle=\frac{1}{\sqrt{2}}(|\alpha_1\beta_2\rangle+|\beta_1\alpha_2\rangle), \tag{2.10c}$$

$$|\Pi_{-1}\rangle=|\beta_1\beta_2\rangle. \tag{2.10e}$$

The dispersion energy of molecules encountering in these eigenstates is [11]

$$U(\Pi_{+1}) = U(\Pi_{-1}) = U_{\alpha_1\alpha_2,\,\alpha_1\alpha_2}, \tag{2.11a}$$

$$U(\Sigma^{\mp}) = U_{\alpha_1\beta_2,\,\alpha_1\beta_2} \pm U_{\alpha_1\beta_2,\,\beta_1\alpha_2}, \tag{2.11b}$$

where

$$U_{m_1m_2,\,n_1n_2} = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 T_{\alpha\beta}\,T_{\gamma\delta} \times \sum_{\substack{j_1\neq n_1,\,m_1\\ j_2\neq n_2,\,m_2}} \frac{\langle m_1 m_2|\mu_{1\alpha}\mu_{2\beta}|j_1 j_2\rangle\langle j_1 j_2|\mu_{1\gamma}\mu_{2\delta}|n_1 n_2\rangle}{\hbar(\omega_{j_1n_1}+\omega_{j_2n_2})}. \tag{2.11c}$$

For simplicity, we have not specified explicitly the spatial parts of the states. Introducing symmetric (+) and antisymmetric (−) *transition* polarizability tensors

$$(\alpha^{+}_{\alpha\beta})_{mn}(\omega) = \frac{1}{\hbar}\sum_{j\neq n,\,m}\frac{\omega_{jn}}{\omega_{jn}^2-\omega^2} \times (\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle + \langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle) = (\alpha^{+}_{\beta\alpha})_{mn}(\omega), \tag{2.12a}$$

$$(\alpha^{-}_{\alpha\beta})_{mn}(\omega) = \frac{i}{\hbar}\sum_{j\neq n,\,m}\frac{\omega}{\omega_{jn}^2-\omega^2} \times (\langle m|\mu_\alpha|j\rangle\langle j|\mu_\beta|n\rangle - \langle m|\mu_\beta|j\rangle\langle j|\mu_\alpha|n\rangle) = -(\alpha^{-}_{\beta\alpha})_{mn}(\omega), \tag{2.12b}$$

we obtain

$$U_{m_1m_2,\,n_1n_2} = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2\left(\frac{\hbar}{2\pi}\right)T_{\alpha\beta}\,T_{\gamma\delta}\int_0^\infty \times [(\alpha^{+}_{1\alpha\gamma})_{m_1n_1}(iu)(\alpha^{+}_{2\beta\delta})_{m_2n_2}(iu) + (\alpha^{-}_{1\alpha\gamma})_{m_1n_1}(iu)(\alpha^{-}_{2\beta\delta})_{m_2n_2}(iu)]\,du. \tag{2.13}$$

The transition polarizabilities (2.12) are not quite as general as corresponding Raman transition polarizabilities [7] because $|n\rangle$ and $|m\rangle$ must have the same, or nearly the same, energy.

If the odd-electron molecules are chiral there will, in addition, be analogous discriminating dispersion interactions for pairs encountering in the singlet and triplet states (2.10). Specifically,

$$U'_{m_1m_2,\,n_1n_2} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar}{\pi}\right)T_{\alpha\beta}\,T_{\gamma\delta}\int_0^\infty \times [(G^{+}_{1\alpha\gamma})_{m_1n_1}(iu)(G^{+}_{2\beta\delta})_{m_2n_2}(iu) + (G^{-}_{1\alpha\gamma})_{m_1n_1}(iu)(G^{-}_{2\beta\delta})_{m_2n_2}(iu)]\,du, \tag{2.14}$$

where

$$(G^{+}_{\alpha\beta})_{mn}(\omega) = \frac{1}{\hbar}\sum_{j\neq n,\,m}\frac{\omega_{jn}}{\omega_{jn}^2-\omega^2} \times (\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle + \langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle), \tag{2.15a}$$

$$(G^{-}_{\alpha\beta})_{mn}(\omega) = \frac{i}{\hbar} \sum_{j \neq n,\, m} \frac{\omega}{\omega_{jn}^2 - \omega^2}$$

$$\times \left(\langle m|\mu_\alpha|j\rangle\langle j|m_\beta|n\rangle - \langle m|m_\beta|j\rangle\langle j|\mu_\alpha|n\rangle \right), \quad (2.15b)$$

are transition optical acitvity tensors. Because products of transition moments containing different operators are involved, these transition optical activities do not have well-defined behaviour under permutation of the tensor subscripts, unlike the transition polarizabilities (2.12).

3. Optical activity and time reversal

Further development of the one-centre contributions (2.13) and (2.14) to the dispersion interaction between odd-electron molecules is facilitated by a consideration of the behaviour of the transition polarizability and optical activity tensors under time reversal.

It is easy to deduce the behaviour under time reversal of the basic polarizability and optical activity tensors (2.6) and (2.9) from simple classical arguments [16, 6, 7] based on a consideration of the contributions of these tensors to the oscillating electric dipole moment induced in a molecule by the electric and magnetic field vectors **E** and **B** of a light wave:

$$\mu_\alpha = \alpha_{\alpha\beta} E_\beta + \frac{1}{\omega} \alpha'_{\alpha\beta} \dot{E}_\beta + G_{\alpha\beta} B_\beta + \frac{1}{\omega} G'_{\alpha\beta} \dot{B}_\beta + \ldots. \quad (3.1)$$

Classical time reversal involves replacing t by $-t$ everywhere, from which it follows that μ_α is time-even so that the real and imaginary polarizabilities $\alpha_{\alpha\beta}$ and $\alpha'_{\alpha\beta}$ must be time-even and time-odd, respectively; whereas the real and imaginary optical activities $G_{\alpha\beta}$ and $G'_{\alpha\beta}$ must be time-odd and time-even. It is the imaginary part $G'_{\alpha\beta}$ that is responsible for conventional optical activity phenomena such as optical rotation: the real part is responsible for exotic effects such as gyrotropic birefringence [17] and magneto-chiral birefringence and dichroism [18] which require the presence of a static magnetic field or some other time-odd influence.

Useful relationships between components of the corresponding transition tensors involving various degenerate states can be deduced from a consideration of the behaviour of states and operators under the quantum-mechanical time reversal operation Θ that first takes the complex conjugate of a wavefunction and then reverses the sign of the time coordinate. The two orthogonal spin states α and β provide an important example: it can be shown that (with a particular choice of phase) [19]

$$\Theta\alpha = \beta, \qquad \Theta\beta = -\alpha. \quad (3.2)$$

Time-even (+) and time-odd (−) operators are defined by

$$\Theta \hat{A}(\pm)\Theta^{-1} = \pm \hat{A}(\pm)^\dagger. \quad (3.3)$$

The transition tensors (2.12) and (2.15) can be generated by taking matrix elements of the corresponding effective operators [7, 9, 12]

$$\hat{\alpha}^{+}_{\alpha\beta} = \tfrac{1}{2}(\mu_\alpha 0^{+} \mu_\beta + \mu_\beta 0^{+} \mu_\alpha), \tag{3.4a}$$

$$\hat{\alpha}^{-}_{\alpha\beta} = -\tfrac{1}{2}(\mu_\alpha 0^{-} \mu_\beta - \mu_\beta 0^{-} \mu_\alpha), \tag{3.4b}$$

and

$$\hat{G}^{+}_{\alpha\beta} = \tfrac{1}{2}(\mu_\alpha 0^{+} m_\beta + m_\beta 0^{+} \mu_\alpha), \tag{3.4c}$$

$$\hat{G}^{-}_{\alpha\beta} = -\tfrac{1}{2}(\mu_\alpha 0^{-} m_\beta - m_\beta 0^{-} \mu_\alpha), \tag{3.4d}$$

where

$$0^{\pm} = \left(\frac{1}{H - \bar{W} + \hbar\omega} \pm \frac{1}{H - \bar{W} - \hbar\omega}\right). \tag{3.4e}$$

$\bar{W}$ is the average of the energies W_n and W_m of the initial and final states. By summing over a complete set of states $|j\rangle\langle j|$ inserted after 0, it is easily verified that

$$(\alpha^{+}_{\alpha\beta})_{mn}(\omega) = \langle m|\hat{\alpha}^{+}_{\alpha\beta}|n\rangle, \tag{3.5a}$$

$$(\alpha^{-}_{\alpha\beta})_{mn}(\omega) = i\langle m|\hat{\alpha}^{-}_{\alpha\beta}|n\rangle, \tag{3.5b}$$

$$(G^{+}_{\alpha\beta})_{mn}(\omega) = \langle m|\hat{G}^{+}_{\alpha\beta}|n\rangle, \tag{3.5c}$$

$$(G^{-}_{\alpha\beta})_{mn}(\omega) = i\langle m|\hat{G}^{-}_{\alpha\beta}|n\rangle. \tag{3.5d}$$

It has been shown that the product of two non-commuting hermitian operators with well-defined behaviour under time reversal does not itself have well-defined behaviour but can be written as the sum of a time-even and a time-odd operator [19]. By extending these considerations to the operators (3.4), it can be shown that $\hat{\alpha}^{+}_{\alpha\beta}$ is time-even and hermitian, $\hat{\alpha}^{-}_{\alpha\beta}$ is time-odd and anti-hermitian, $\hat{G}^{+}_{\alpha\beta}$ is time-odd and hermitian, and $\hat{G}^{-}_{\alpha\beta}$ is time-even and anti-hermitian [7, 12]. Then using the result [19, 7]

$$\langle \Theta a|\hat{A}(\pm)|\Theta b\rangle = \pm\langle b|\hat{A}(\pm)|a\rangle, \tag{3.6}$$

we obtain the following general relationships:

$$(\alpha^{+}_{\alpha\beta})_{mn} = (\alpha^{+}_{\alpha\beta})_{\Theta n\Theta m} = (\alpha^{+}_{\alpha\beta})^{*}_{\Theta m\Theta n}, \tag{3.7a}$$

$$(\alpha^{-}_{\alpha\beta})_{mn} = -(\alpha^{-}_{\alpha\beta})_{\Theta n\Theta m} = -(\alpha^{-}_{\alpha\beta})^{*}_{\Theta m\Theta n}, \tag{3.7b}$$

$$(G^{+}_{\alpha\beta})_{mn} = -(G^{+}_{\alpha\beta})_{\Theta n\Theta m} = -(G^{+}_{\alpha\beta})^{*}_{\Theta m\Theta n}, \tag{3.7c}$$

$$(G^{-}_{\alpha\beta})_{mn} = (G^{-}_{\alpha\beta})_{\Theta n\Theta m} = (G^{-}_{\alpha\beta})^{*}_{\Theta m\Theta n}. \tag{3.7d}$$

Chiu [20] has also used time reversal arguments to discuss aspects of natural optical activity in degenerate states, but his approach is rather different.

In what follows, we use the terms time-even and time-odd transition tensors to refer to tensors generated by time-even and time-odd operators, respectively. This terminology is rather loose, because the behaviour of the associated matrix element is only that of the operator for diagonal transitions.

An important characteristic of these transition tensors is the existence or otherwise of a static limit. Thus the transition tensors generated by the *hermitian* operators $\hat{\alpha}^{+}_{\alpha\beta}$ and $\hat{G}^{+}_{\alpha\beta}$ remain finite as $\omega \to 0$, whereas those generated by the *anti-hermitian* operators $\hat{\alpha}^{-}_{\alpha\beta}$ and $\hat{G}^{-}_{\alpha\beta}$ vanish. We shall see that this has important consequences for chiral discrimination in the wave-zone limit.

4. The singlet and triplet dispersion energy

We now apply the results of the previous section to simplify expressions for the singlet and triplet dispersion energy of pairs of chiral molecules in twofold Kramers-degenerate states. Using (3.2) in (3.7), we find for the transition polarizability

$$(\alpha^{+}_{\alpha\beta})_{\pm 1/2 \pm 1/2}(\omega) = (\alpha^{+}_{\alpha\beta})_{\mp 1/2 \mp 1/2}(\omega), \tag{4.1 a}$$

$$(\alpha^{-}_{\alpha\beta})_{\pm 1/2 \pm 1/2}(\omega) = -(\alpha^{-}_{\alpha\beta})_{\mp 1/2 \mp 1/2}(\omega), \tag{4.1 b}$$

$$(\alpha^{+}_{\alpha\beta})_{\pm 1/2 \mp 1/2}(\omega) = -(\alpha^{+}_{\alpha\beta})^{*}_{\mp 1/2 \pm 1/2}(\omega), \tag{4.1 c}$$

$$(\alpha^{-}_{\alpha\beta})_{\pm 1/2 \mp 1/2}(\omega) = (\alpha^{-}_{\alpha\beta})^{*}_{\mp 1/2 \pm 1/2}(\omega). \tag{4.1 d}$$

Similarly, we find for the transition optical activity

$$(G^{+}_{\alpha\beta})_{\pm 1/2 \pm 1/2}(\omega) = -(G^{+}_{\alpha\beta})_{\mp 1/2 \mp 1/2}(\omega), \tag{4.1 e}$$

$$(G^{-}_{\alpha\beta})_{\pm 1/2 \pm 1/2}(\omega) = (G^{-}_{\alpha\beta})_{\mp 1/2 \mp 1/2}(\omega), \tag{4.1 f}$$

$$(G^{+}_{\alpha\beta})_{\pm 1/2 \mp 1/2}(\omega) = (G^{+}_{\alpha\beta})^{*}_{\mp 1/2 \pm 1/2}(\omega), \tag{4.1 g}$$

$$(G^{-}_{\alpha\beta})_{\pm 1/2 \mp 1/2}(\omega) = -(G^{-}_{\alpha\beta})^{*}_{\mp 1/2 \pm 1/2}(\omega). \tag{4.1 h}$$

The polarizability dispersion energy contributions are then

$$\begin{aligned} U(\Pi_{+}) = U(\Pi_{-}) &= -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \left(\frac{\hbar}{2\pi}\right) T_{\alpha\beta}\, T_{\gamma\delta} \int_0^\infty \\ &\quad \times [(\alpha^{+}_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(\alpha^{+}_{2_{\beta\delta}})_{+1/2+1/2}(iu) \\ &\quad + (\alpha^{-}_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(\alpha^{-}_{2_{\beta\delta}})_{+1/2+1/2}(iu)]\, du, \end{aligned} \tag{4.2 a}$$

$$\begin{aligned} U(\Sigma^{\mp}) = &-\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \left(\frac{\hbar}{2\pi}\right) T_{\alpha\beta}\, T_{\gamma\delta} \int_0^\infty \\ &\times [(\alpha^{+}_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(\alpha^{+}_{2_{\beta\delta}})_{+1/2+1/2}(iu) \\ &- (\alpha^{-}_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(\alpha^{-}_{2_{\beta\delta}})_{+1/2+1/2}(iu) \\ &\mp (\alpha^{+}_{1_{\alpha\gamma}})_{+1/2-1/2}(iu)(\alpha^{+}_{2_{\beta\delta}})^{*}_{+1/2-1/2}(iu) \\ &\pm (\alpha^{-}_{1_{\alpha\gamma}})_{+1/2-1/2}(iu)(\alpha^{-}_{2_{\beta\delta}})^{*}_{+1/2-1/2}(iu)]\, du, \end{aligned} \tag{4.2 b}$$

and the discriminating optical activity contributions are

$$U'(\Pi_+) = U'(\Pi_-)$$
$$= -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar}{\pi}\right)T_{\alpha\beta}\,T_{\gamma\delta}\int_0^\infty$$
$$\times\ [(G^+_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(G^+_{2_{\beta\delta}})_{+1/2+1/2}(iu)$$
$$+\ (G^-_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(G^-_{2_{\beta\delta}})_{+1/2+1/2}(iu)]\ du, \tag{4.2c}$$

$$U'(\Sigma^\mp) = -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar}{\pi}\right)T_{\alpha\beta}\,T_{\gamma\delta}\int_0^\infty$$
$$\times\ [-(G^+_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(G^+_{2_{\beta\delta}})_{+1/2+1/2}(iu)$$
$$+\ (G^-_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(G^-_{2_{\beta\delta}})_{+1/2+1/2}(iu)$$
$$\pm\ (G^+_{1_{\alpha\gamma}})_{+1/2-1/2}(iu)(G^+_{2_{\beta\delta}})^*_{+1/2-1/2}(iu)$$
$$\mp\ (G^-_{1_{\alpha\gamma}})_{+1/2-1/2}(iu)(G^-_{2_{\beta\delta}})^*_{+1/2-1/2}(iu)]\ du. \tag{4.2d}$$

Notice that the contributions from the time-odd tensors $\alpha^-_{\alpha\beta}$ and $G^+_{\alpha\beta}$ disappear when summed over the singlet and the three triplet states.

In general, the calculation of optical activity parameters for specific chiral molecules is difficult and the results often unreliable. However, it is possible to calculate meaningful *relative* magnitudes of the time-odd and time-even contributions to the chiral discrimination because the interference terms that the chiral distortion induces between the electric and magnetic dipole transition moments have the same reduced matrix elements in the two contributions. It is instructive to take as a model a hypothetical chiral odd-electron transition metal complex of symmetry O^*. Large spin–orbit coupling in the charge-transfer states of iridium (IV) hexahalide complexes generates significant antisymmetric scattering contributions to resonance Raman processes from the time-odd part of the transition polarizability $(\alpha^-_{\alpha\beta})_{mn}$ [7, 9, 10], and similar mechanisms will generate time-odd transition optical activity components $(G^+_{\alpha\beta})_{mn}$ in corresponding chiral complexes.

We take the same pattern of spin–orbit levels as is found in $IrBr_6^{2-}$ in aqueous solution (figure) [21]. The first few electric dipole-allowed transitions in the parent O_h^* complex are

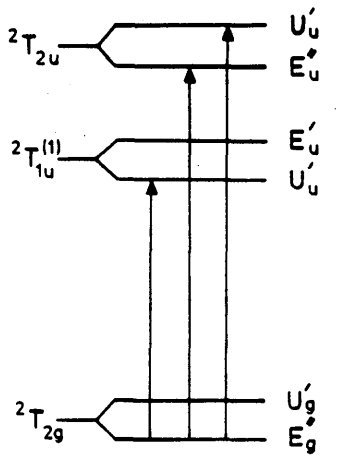
$$U'_u(^2T^{(1)}_{1u}) \leftarrow E''_g(^2T_{2g}),\quad E''_u(^2T_{2u}) \leftarrow E''_g(^2T_{2g}) \quad \text{and} \quad U'_u(^2T_{2u}) \leftarrow E''_g(^2T_{2g}).$$

These all become magnetic dipole-allowed as well in the hypothetical chiral O^* complex. The first transition $U'_g(^2T_{2g}) \leftarrow E''_g(^2T_{2g})$ is forbidden because both terms originate in the same orbital configuration. Using Harnung's version of the Wigner–Eckart theorem for the octahedral double group O^* [22, 7], we find the following transition polarizability and optical activity tensor patterns:

(*a*) E'' intermediate level

(i) $(\alpha^+_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| E''(j)\rangle|^2 \omega_{jn}/\hbar(\omega^2_{jn} - \omega^2)$



The first few electric dipole-allowed transitions between the spin–orbit levels of $[IrBr_6]^{2-}$.

$$\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix}\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (4.3\,a)$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(ii) $(\alpha^-_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| E''(j)\rangle|^2 \omega/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} 0 & \frac{1}{3} & 0 \\ -\frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & -\frac{1}{3} & 0 \\ \frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & \frac{i}{3} \\ 0 & 0 & \frac{1}{3} \\ -\frac{i}{3} & -\frac{1}{3} & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & -\frac{i}{3} \\ 0 & 0 & \frac{1}{3} \\ \frac{i}{3} & -\frac{1}{3} & 0 \end{pmatrix} \qquad (4.3\,b)$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(iii) $(G^+_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| E''(j)\rangle| \, |\langle E''(n) \| m \| E''(j)\rangle| \, \omega_{jn}/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} 0 & \frac{1}{3} & 0 \\ -\frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & -\frac{1}{3} & 0 \\ \frac{1}{3} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & \frac{i}{3} \\ 0 & 0 & \frac{1}{3} \\ -\frac{i}{3} & -\frac{1}{3} & 0 \end{pmatrix}\begin{pmatrix} 0 & 0 & -\frac{i}{3} \\ 0 & 0 & \frac{1}{3} \\ \frac{i}{3} & -\frac{1}{3} & 0 \end{pmatrix} \qquad (4.3\,c)$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(iv) $(G^-_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| E''(j)\rangle| \, |\langle E''(n) \| m \| E''(j)\rangle| \, \omega/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4.3d}$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(*b*) U' intermediate level

(i) $(\alpha^{+}_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| U'(j)\rangle|^2 \omega_{jn}/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4.3e}$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(ii) $(\alpha^{-}_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| U'(j)\rangle|^2 \omega/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} 0 & -\frac{1}{6} & 0 \\ \frac{1}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{6} & 0 \\ -\frac{1}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & -\frac{i}{6} \\ 0 & 0 & -\frac{1}{6} \\ \frac{i}{6} & \frac{1}{6} & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & \frac{i}{6} \\ 0 & 0 & -\frac{1}{6} \\ -\frac{i}{6} & \frac{1}{6} & 0 \end{pmatrix} \tag{4.3f}$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(iii) $(G^{+}_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n) \| \mu \| U'(j)\rangle| \, |\langle E''(n) \| m \| U'(j)\rangle| \, \omega_{jn}/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} 0 & -\frac{1}{6} & 0 \\ \frac{1}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & \frac{1}{6} & 0 \\ -\frac{1}{6} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & -\frac{i}{6} \\ 0 & 0 & -\frac{1}{6} \\ \frac{i}{6} & \frac{1}{6} & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & \frac{i}{6} \\ 0 & 0 & -\frac{1}{6} \\ -\frac{i}{6} & \frac{1}{6} & 0 \end{pmatrix} \tag{4.3g}$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

(iv) $(G^{-}_{\alpha\beta})_{mn}$

Common factor $|\langle E''(n)| \, |\mu \| U'(j)\rangle| \, |\langle E''(m) \| m \| U'(j)\rangle| \, \omega/\hbar(\omega_{jn}^2 - \omega^2)$

$$\begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{4.3h}$$

$$+\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow -\tfrac{1}{2} \quad -\tfrac{1}{2} \leftarrow +\tfrac{1}{2} \quad +\tfrac{1}{2} \leftarrow -\tfrac{1}{2}$$

We have assumed that the electric and magnetic dipole moment reduced matrix elements are pure real and pure imaginary, respectively. Notice that these tensor components accord with the relationships (4.1).

An interesting feature of these transition tensor components is that, unlike the case of atomic Na where the contributions to the time-odd (antisymmetric) transition polarizability $(\alpha^-_{\alpha\beta})_{mn}$ associated with transitions from the ground level to the spin–orbit split components of a given excited level (e.g. $^2P_{1/2}$, $^2P_{3/2} \leftarrow {}^2S_{1/2}$) would sum to zero if the splitting were zero [11], the corresponding contributions in $IrBr_6^{2-}$ do not cancel. For example, it has been shown that [23, p.488]

$$|\langle E''_g(^2T_{2g}) \| \mu \| E''_u(^2T_{2u})\rangle|^2 = 2|\langle E''_g(^2T_{2g}) \| \mu \| U'_u(^2T_{2u})\rangle|^2 \tag{4.4}$$

and so from (4.3 *b*) and (4.3 *f*) we see that the contributions to $(\alpha^-_{\alpha\beta})_{mn}$ from the pair of spin–orbit components E''_u and U'_u deriving from the excited level $^2T_{2u}$ (figure) would by no means sum to zero. Indeed, looking at the spin–orbit components U'_u and E'_u deriving from the $^2T^{(1)}_{1u}$ excited level, we see that there is no cancellation at all since only U'_u contributes to $(\alpha^-_{\alpha\beta})_{mn}$, transitions to E'_u being electric dipole-forbidden. In order to obtain a rough estimate of the relative magnitudes of the contributions from the time-even and the time-odd transition tensors to the dispersion interaction we shall therefore consider, for simplicity, just the $U'_u(^2T^{(1)}_{1u})$ excited level.

For the situation where the two interacting molecules are held in fixed orientations relative to each other, we refer the property tensors of each to a common axis system X, Y, Z attached to the pair. Taking Z to be along the vector $\mathbf{R}$ connecting the two local origins, we have from (2.2 *c*)

$$\begin{aligned} T_{\alpha\beta}\, T_{\gamma\delta}\, G_{1_{\alpha\gamma}}\, G_{2_{\beta\delta}} = R^{-6}[&G_{1XX}\, G_{2XX} + G_{1YY}\, G_{2YY} + 4G_{1ZZ}\, G_{2ZZ} \\ &+ G_{1XY}\, G_{2XY} + G_{1YX}\, G_{2YX} \\ &- 2(G_{1XZ}\, G_{2XZ} + G_{1ZX}\, G_{2ZX} \\ &+ G_{1YZ}\, G_{2YZ} + G_{1ZY}\, G_{2ZY})]. \end{aligned} \tag{4.5}$$

If the principal axes of the two molecules have different orientations with respect to the reference axes, $G_{1_{\alpha\beta}}$ will not in general be the same as $G_{2_{\alpha\beta}}$. But for simplicity we take the case where the principal axes of the two molecules have the same orientations. Considering just the $U'(^2T^{(1)}_{1u})$ excited level (the subscripts 'g' and 'u' are retained in the orbital term symbols to indicate the O^*_h parentage of the spin–orbit levels in O^*) we use (2.4), (4.3 *g*), (4.3 *h*) and (4.5) to write

$$T_{\alpha\beta}\, T_{\gamma\delta} \int_0^\infty (G^+_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(G^+_{2_{\beta\delta}})_{+1/2+1/2}(iu)\, du$$

$$= \frac{\pi}{72\hbar^2 R^6 \omega_{u'}} |\langle E''(^2T_{2g}) \| \mu \| U'(^2T^{(1)}_{1u})\rangle|^2 |\langle E''(^2T_{2g}) \| m \| U'(^2T^{(1)}_{1u})\rangle|^2, \tag{4.6a}$$

$$T_{\alpha\beta}\, T_{\gamma\delta} \int_0^\infty (G^-_{1_{\alpha\gamma}})_{+1/2+1/2}(iu)(G^-_{2_{\beta\delta}})_{+1/2+1/2}(iu)\, du$$

$$= -\frac{\pi}{6\hbar^2 R^6 \omega_{u'}} |\langle E''(^2T_{2g}) \| \mu \| U'(^2T^{(1)}_{1u})\rangle|^2 |\langle E''(^2T_{2g}) \| m \| U'(^2T^{(1)}_{1u})\rangle|^2, \tag{4.6b}$$

etc. The total discriminatory dispersion energy may now be written $U' = U'_0(1 + \lambda'/4)$, where λ' characterizes the additional contributions from the time-odd tensors and takes the values -1, $-\frac{1}{3}$, $\frac{5}{3}$ for the states $|\Sigma^+\rangle$, $|\Pi_{\pm 1}\rangle$, $|\Sigma^-\rangle$, respectively, and

$$U'_0 = \left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\frac{1}{6\hbar R^6\omega_{u'}} \times |\langle E''(^2T_{2g}) \| \mu \| U'(^2T_{1u}^{(1)})\rangle|^2 |\langle E''(^2T_{2g}) \| m \| U'(^2T_{1u}^{(1)})\rangle|^2. \quad (4.7a)$$

Similarly, the total non-discriminatory dispersion energy may be written $U = U_0(1 + \lambda/4)$, where λ characterizes the additional contributions from the time-odd tensors taking the same values as λ' above, and

$$U_0 = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \frac{1}{12\hbar R^6\omega_{u'}} |\langle E''(^2T_{2g}) \| \mu \| U'(^2T_{1u}^{(1)})\rangle|^4. \quad (4.7b)$$

The sign difference between U_0 and U'_0 reflects the fact that the conventional contribution (i.e. from time-even tensors) to the non-discriminatory dispersion interaction is attractive (negative), whereas the conventional contribution to the discriminatory dispersion interaction is repulsive (positive) between pairs of chiral molecules of the same species and same enantiomer provided the two molecules have the same orientation relative to the reference axes [2, 5, 15].

The results of our model calculation indicate that contributions from time-odd tensors to the dispersion energy, both non-discriminatory and discriminatory, could be within an order of magnitude of the conventional contributions from time-even tensors for pairs of molecules with large spin–orbit coupling. This contrasts with the case of interacting pairs of alkali metal atoms, where the additional contributions are expected to be four orders of magnitude smaller in the most favourable cases [11]. Notice, however, that the sum of the contributions from the time-odd tensors over the four possible states $|\Sigma^{\pm}\rangle$ and $|\Pi_{\pm 1}\rangle$ of the interacting pair is zero, as anticipated quite generally from (4.2).

The isotropic case, where the molecules are free to rotate relative to each other, requires further consideration. In atoms, the 'molecule-fixed' axes can be chosen to coincide with the space-fixed axes so that orientational averaging is irrelevant; and, as discussed by Piepho and Schatz [23, p. 89], this is usually also the case for molecules belonging to the cubic point groups since the Zeeman effect is usually isotropic. This implies that the above results for oriented molecules of cubic symmetry should correlate with the isotropic case. Thus averaging each tensor component in (4.5) independently using isotropic averages such as $\langle\alpha_{\alpha\beta}\rangle = \alpha\delta_{\alpha\beta}$, where $\alpha = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ})$, we recover the same dispersion energies as before, but summed over the singlet and three triplet spin states so that the contributions from the time-odd tensors in $U = U_0(1 + \lambda/4)$ and $U' = U'_0(1 + \lambda'/4)$ vanish (this corresponds to the fact that each time-odd tensor component has a zero classical isotropic average).

5. The wave-zone limit: retardation effects

At separations much larger than the wavelengths of the molecular transitions, the finite speed of propagation of light leads to a cancellation of the ordinary

dispersion energy varying as R^{-6}, being replaced by an interaction dominated by a term varying as R^{-7} [24]. This Casimir–Polder potential is derived using quantum electrodynamics.

We consider first just the contributions from time-even tensors. Thus starting from equation (7.4.9) of Craig and Thirunamachandran [5] and retaining only the terms corresponding to contributions from virtual photons with energies much less than the molecular transition energies, the wave-zone non-discriminatory dispersion energy is found to be

$$U_{m_1m_2,\,n_1n_2} = -\left(\frac{1}{4\pi\varepsilon_0}\right)^2\left(\frac{\hbar c}{8\pi R^7}\right)$$
$$\times\,(3R^2S_{\alpha\gamma}S_{\beta\delta} - 5R^4S_{\alpha\gamma}T_{\beta\delta} + 5R^6T_{\alpha\gamma}T_{\beta\delta})(\alpha^+_{\alpha\beta})^{\mathrm{SL}}_{m_1n_1}(\alpha^+_{\gamma\delta})^{\mathrm{SL}}_{m_2n_2}, \quad (5.1)$$

where

$$S_{\alpha\beta} = \nabla_\alpha\nabla_\beta R = (R^2\delta_{\alpha\beta} - R_\alpha R_\beta)R^{-3}$$

and we have generalized to a transition energy as in (2.13). The superscript SL indicates the static limit ($\omega \to 0$) of the tensor. In the isotropic case where the two molecules are free to rotate independently, this expression reduces to the usual Casimir–Polder expression if $m = n$ [5, 24]

$$U = -\frac{23\hbar c}{64\pi^3\varepsilon_0^2 R^7}\alpha_1^{\mathrm{SL}}\alpha_2^{\mathrm{SL}}. \quad (5.2)$$

Similarly, the discriminatory dispersion energy between a pair of chiral molecules at the wave-zone separation is

$$U'_{m_1m_2,\,n_1n_2} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar^3c^3}{8\pi R^9}\right)\Big\{[14R^6T_{\alpha\gamma}T_{\beta\delta}$$
$$- 21R^4(T_{\alpha\gamma}S_{\beta\delta} + S_{\alpha\gamma}T_{\beta\delta}) + 45R^2S_{\alpha\gamma}S_{\beta\delta} + 81\varepsilon_{\alpha\gamma\mu}\varepsilon_{\delta\beta\lambda}R_\mu R_\lambda R^{-2}]$$
$$\times \sum_{j_1}\frac{1}{\hbar^2\omega^2_{j_1n_1}}(\langle m_1|\mu_{1_\alpha}|j_1\rangle\langle j_1|m_{1_\beta}|n_1\rangle - \langle m_1|m_{1_\beta}|j_1\rangle\langle j_1|\mu_{1_\alpha}|n_1\rangle)$$
$$\times \sum_{j_2}\frac{1}{\hbar^2\omega^2_{j_2n_2}}(\langle m_2|\mu_{2_\gamma}|j_2\rangle\langle j_2|m_{2_\delta}|n_2\rangle - \langle m_2|m_{2_\delta}|j_2\rangle\langle j_2|\mu_{2_\gamma}|n_2\rangle)$$
$$- [14R^6T_{\alpha\gamma}T_{\beta\delta} - 21R^4(T_{\alpha\gamma}S_{\beta\delta} + S_{\alpha\gamma}T_{\beta\delta}) + 45R^2S_{\alpha\gamma}S_{\beta\delta}$$
$$- 81\varepsilon_{\alpha\gamma\mu}\varepsilon_{\delta\beta\lambda}R_\mu R_\lambda R^{-2}]\sum_{j_1j_2}\frac{\omega^2_{j_1n_1} + \omega^2_{j_2n_2}}{\hbar^4\omega^2_{j_1n_1}\omega^2_{j_2n_2}}$$
$$\times (\langle m_1|\mu_{1_\alpha}|j_1\rangle\langle j_1|m_{1_\beta}|n_1\rangle + \langle m_1|m_{1_\beta}|j_1\rangle\langle j_1|\mu_{1_\alpha}|n_1\rangle)$$
$$\times (\langle m_2|\mu_{2_\gamma}|j_2\rangle\langle j_2|m_{2_\delta}|n_2\rangle + \langle m_2|m_{2_\delta}|j_2\rangle\langle j_2|\mu_{2_\delta}|n_2\rangle)\Big\}. \quad (5.3)$$

Again, in the isotropic case with $m = n$, this reduces to a standard expression [5]

$$U' = \left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{16\hbar^3c^3}{3\pi R^9}\right) \times \sum_{j_1} \frac{1}{\hbar^2\omega_{j_1n_1}^2} \operatorname{Im}\left(\langle n_1|\mu_{1_\alpha}|j_1\rangle\langle j_1|m_{1_\alpha}|n_1\rangle\right) \times \sum_{j_2} \frac{1}{\hbar^2\omega_{j_2n_2}^2} \operatorname{Im}\left(\langle n_2|\mu_{2_\beta}|j_2\rangle\langle j_2|m_{2_\beta}|n_2\rangle\right). \tag{5.4}$$

We now consider the new contributions from time-odd tensors. Unlike the near-zone situation, these have a different R-dependence from the corresponding time-even tensors. Thus there is a non-discriminatory term looking similar to (5.3) but involving only electric dipole interactions [25]: we have not bothered to write it down because the dependence on R^{-9} ensures that it will usually be of no significance relative to the conventional contribution (5.1). On the other hand, the contribution from time-odd tensors to the discriminatory dispersion interaction looks similar to (5.1), including a dependence on R^{-7}

$$U'_{m_1m_2,n_1n_2} = -\left(\frac{1}{4\pi\varepsilon_0}\right)\left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar c}{8\pi R^7}\right)[10R^6T_{\alpha\gamma}T_{\beta\delta} - 5R^4(T_{\alpha\gamma}S_{\beta\delta} + S_{\alpha\gamma}T_{\beta\delta}) + 6R^2S_{\alpha\gamma}S_{\beta\delta} - 14\varepsilon_{\alpha\delta\mu}\varepsilon_{\alpha\beta\lambda}R_\mu R_\lambda R^{-2}](G_{1_{\alpha\beta}}^{+})_{m_1n_1}^{\mathrm{SL}}(G_{2_{\gamma\delta}}^{+})_{m_2n_2}^{\mathrm{SL}}. \tag{5.5}$$

Since the conventional wave-zone discriminatory dispersion energy (5.3) depends on R^{-9}, this additional contribution between odd-electron chiral molecules could be several orders of magnitude larger.

A full quantum-electrodynamical treatment that gives complete expressions containing both time-even and time-odd tensors in the near zone and the wave zone (including some other new terms) is given elsewhere [25].

6. Discussion

We have shown that, in favourable cases, there are additional contributions to the discriminating dispersion interaction between odd-electron chiral molecules encountering in spin eigenstates of the interacting pair that are within an order of magnitude of the conventional contribution. In the near zone these new contributions, which originate in the time-odd part of the molecular optical activity tensor, have the same R^{-6} dependence as the conventional contributions arising from the time-even part. But in the wave zone, the new discriminating contributions depend on R^{-7}, unlike the conventional discriminating contributions which depend on R^{-9}: this is because the time-even part $(G_{\alpha\beta}^{-})_{mn}$ of the optical activity tensor does not have a static limit (like the time-odd part $(\alpha_{\alpha\beta}^{-})_{mn}$ of the polarizability tensor), whereas the time-odd part $(G_{\alpha\beta}^{+})_{mn}$ does have a static limit (like the time-even part $(\alpha_{\alpha\beta}^{+})_{mn}$ of the polarizability tensor).

Unfortunately these new discriminating contributions mutually cancel when summed over the singlet and the three triplet eigenstates of the interacting pair. However, since the dispersion interaction lifts some of the degeneracy of these states (we have seen that $\Sigma^{\mp}$ split apart), there should be a small residual effect arising

from population differences. In the hypothetical chiral O^* complex considered above, this would reduce the conventional repulsive discriminating contribution to the dispersion interaction between pairs of chiral molecules of the same enantiomer and reduce the attractive discriminating contribution between pairs of opposite enantiomers. On the other hand there is the interesting possibility of manipulating the discriminating dispersion interaction with a magnetic field: since the field would split the $\Pi_{\pm 1}$ states, we would expect the effects described in the previous sentence to be enhanced.

The magnetic field dependence of the wave zone discriminating dispersion interactions in R^{-7} could have interesting consequences in biological systems.

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References

[1] MASON, S. F., 1982, *Molecular Optical Activity and the Chiral Discriminations* (Cambridge University Press).
[2] CRAIG, D. P., and MELLOR, D. P., 1976, *Topics Curr. Chem.*, **63**, 1.
[3] MASON, S. F. (editor), 1979, *Optical Activity and Chiral Discrimination*, NATO ASI Series C (Reidel).
[4] CHIU, Y. N., KENNEY, A. V., and BROWN, S. H., 1980, *J. chem. Phys.*, **73**, 1422.
[5] CRAIG, D. P., and THIRUNAMACHANDRAN, T., 1984, *Molecular Quantum Electrodynamics* (Academic Press).
[6] BUCKINGHAM, A. D., 1979, *Phil. Trans. R. Soc.* A, **293**, 239.
[7] BARRON, L. D., 1982, *Molecular Light Scattering and Optical Activity* (Cambridge University Press).
[8] STEDMAN, G. E., 1985, *Adv. Phys.*, **34**, 513.
[9] BARRON, L. D., and NØRBY SVENDSEN, E., 1981, *Advances in Infrared and Raman Spectroscopy*, Vol. 8, edited by R. J. H. Clark and R. E. Hester (Heyden), p. 322.
[10] HAMAGUCHI, H., 1985, *Advances in Infrared and Raman Spectroscopy*, Vol. 12, edited by R. J. H. Clark and R. E. Hester (Wiley Heyden), p. 273.
[11] BUCKINGHAM, A. D., and JOSLIN, C. G., 1981, *Chem. Phys. Lett.*, **80**, 615.
[12] BARRON, L. D., 1981, *Molec. Phys.*, **43**, 1395.
[13] BUCKINGHAM, A. D., 1978, *Intermolecular Interactions*, edited by B. Pullman (Wiley), p. 1.
[14] MAVROYANNIS, C., and STEPHEN, M. J., 1962, *Molec. Phys.*, **5**, 629.
[15] CRAIG, D. P., POWER, E. A., and THIRUNAMACHANDRAN, T., 1971, *Proc. R. Soc.* A, **322**, 165.
[16] BUCKINGHAM, A. D., GRAHAM, C., and RAAB, R. E., 1971, *Chem. Phys. Lett.*, **8**, 622.
[17] HORNREICH, R. M., and SHTRIKMAN, S., 1968, *Phys. Rev.*, **171**, 1065.
[18] BARRON, L. D., and VRBANCICH, J., 1984, *Molec. Phys.*, **51**, 715.
[19] ABRAGAM, A., and BLEANEY, B., 1970, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press).
[20] CHIU, Y. N., 1985, *Phys. Rev.* A, **32**, 2257.
[21] HENNING, G. N., MCCAFFERY, A. J., SCHATZ, P. N., and STEPHENS, P. J., 1968, *J. chem. Phys.*, **48**, 5656.
[22] HARNUNG, S. E., 1973, *Molec. Phys.*, **26**, 473.
[23] PIEPHO, S. B., and SCHATZ, P. N., 1983, *Group Theory in Spectroscopy* (Wiley).
[24] CASIMIR, H. B. G., and POLDER, D., 1948, *Phys. Rev.*, **73**, 360.
[25] JOHNSTON, C. J., 1987, Doctoral Thesis, Glasgow University.

Colophon

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